PB-238 834

DEVELOPMENT DOCUMENT FOR EFFLUENT LIMITATIONS GUIDELINES AND NEW SOURCE PERFORMANCE STANDARDS FOR THE COPPER, NICKEL, CHROMIUM, AND ZINC SEGMENT OF THE ELECTROPLATING POINT SOURCE CATEGORY

ENVIRONMENTAL PROTECTION AGENCY

MARCH 1974

DISTRIBUTED BY:

NTIS
National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

BIBLIOGRAPHIC DATA SHEET

1. Report No. EPA-440/1-74-003-a

2.

PB 238 834

4. Title and Subtitle
Development Document for Effluent Limitations Guidelines and New Source Performance Standards for the Copper, Nickel, Chromium, and Zinc Segment of the Electroplating Point Source Category.

5. Report Date
March 1974

6.

7. Author(s)
Kit R. Krickenberger

8. Performing Organization Rept. No.
EPA-440/1-74-003-a

9. Performing Organization Name and Address
Environmental Protection Agency
Effluent Guidelines Division
WSM-E, Rm. 913, WH-452

10. Project/Task/Work Unit No.
NA

11. Contract/Grant No.
68-01-0592

12. Sponsoring Organization Name and Address
Same as #9.

13. Type of Report & Period Covered
Final

14.

15. Supplementary Notes

16. Abstracts
This document presents the findings of an extensive study of the electroplating industry by the Environmental Protection Agency for the purpose of developing effluent limitations guidelines, standards of performance, and pretreatment standards for the industry to implement Sections 304(b) and 306 of the "Act."

Effluent limitations guidelines are set forth for the degree of effluent reduction attainable through the application of the "Best Practicable Control Technology Currently Available" and the "Best Available Technology Economically Achievable" which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The "Standards of Performance for New Sources" set forth a degree of effluent reduction which is achievable through the application of the best available demonstrated control technology processes, operating methods or other alternatives.

17. Key Words and Document Analysis. 17a. Descriptors

PRICES SUBJECT TO CHANGE

17b. Identifiers/Open-Ended Terms

Reproduced by
NATIONAL TECHNICAL
INFORMATION SERVICE
US Department of Commerce
Springfield, VA. 22151

17c. COSATI Field/Group

18. Availability Statement
GPO, Washington, DC

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page)
UNCLASSIFIED

21. No. of Pages
220

22. Price
4.90

DEVELOPMENT DOCUMENT

for

EFFLUENT LIMITATIONS GUIDELINES

and

NEW SOURCE PERFORMANCE STANDARDS

for the

COPPER, NICKEL, CHROMIUM, AND ZINC SEGMENT OF THE ELECTROPLATING POINT SOURCE CATEGORY

Russell E. Train
Administrator

Roger Strelow
Acting Assistant Administrator for Air & Water Programs

Allen Cywin
Director, Effluent Guidelines Division

Kit R. Krickenberger
Project Officer

March 1974

Effluent Guidelines Division
Office of Air and Water Programs
U.S. Environmental Protection Agency
Washington, D.C. 20460

For sale by the Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402

ABSTRACT

This document presents the findings of an extensive study of the electroplating industry by the Environmental Protection Agency for the purpose of developing effluent limitations guidelines, standards of performance, and pretreatment standards for the industry to implement Sections 304(b) and 306 of the "Act."

Effluent limitations guidelines for the copper, nickel, chromium, and zinc segment contained herein set forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best available technology economically achievable which must be achieved by existing point sources by July 1, 1977 and July 1, 1983, respectively. The standards of performance for new souces contained herein set forth the degree of effluent reduction which is achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives. The proposed regulations for all three levels of technology set forth above are presented in Section II, RECOMMENDATIONS.

Supportive data and rationale for development of the proposed effluent limitations guidelines and standards of performance are contained in this report.

CONTENTS

Section		Page
I	CONCLUSIONS	1
II	RECOMMENDATIONS	3
	Best Practicable Control Technology Currently Available	3
	Best Available Technology Economically Achievable	3
	New Source Performance Standards	3
III	INTRODUCTION	7
	Purpose and Authority	7
	Summary of Methods Used for Development of the Effluent Limitations Guidelines and Standards of Performance	8
	Information Sources	9
	General Description of the Electroplating Industry	9
IV	INDUSTRY CATEGORIZATION	13
	Introduction	13
	Objectives of Categorization	13
	The Relationship of Electroplating and Metal Finishing	13
	Profile of Production Processes	13
	Materials Receiving Electroplates	19
	Factors Considered in Categorization	20
V	WASTE CHARACTERIZATION	29
	Introduction	29
	Specific Water Uses	32
	Quantity of Wastes	33
	Sources of Waste	
VI	SELECTION OF POLLUTANT PARAMETERS	49
	Introduction	49
	Metal Finishing Wastewater Constituents	49
	Electroplating Wastewater Constituents	49
	Wastewater Constituents and Parameters of Pollutional Significance	52
	Rationale for the Selection of Wastewater Constituents and Parameters	52
	Rationale for the Selection of Total Metal as A Pollutant Parameter	54
	Rationale for Rejection of Other Wastewater Constituents as Pollutants	57
VII	CONTROL AND TREATMENT TECHNOLOGY	61
	Introduction	61
	Chemical Treatment Technology	61

Preceding page blank

Unit Operations 66
Practical Operating Systems 73
Precipitation of Metal Sulfides 75

Water Conservation Through Control Technology 77

Methods of Achieving No Discharge of Pollutants 168

VIII COST, ENERGY, AND NONWATER QUALITY ASPECTS 113
Introduction 113
Treatment and Control Costs 113
Cost Effectiveness and Treating Procedures 118
Nonwater Quality Aspects 119

IX BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, GUIDELINES, AND LIMITATIONS 123
Introduction 123
Industry Category and Subcategory Covered
Identification of Best Practicable Control Technology Currently Available 124
Rationale for Selecting the Best Practicable Control Technology Currently Available 126
Waste Management Techniques Considered Normal Practice in the Electroplating Industry 126
Degree of Pollution Reduction Based on Existing Performance by Plants of Various, Sizes, Ages, and Processes Using Various Control and Treatment Technology 127
Determination of Effluent Limitations Selection of Best Practicable 163
Additional Factors Considered in Selection of Best Practicable Control Technology Currently Available 167
Guidelines for the Application of Effluent Limitations 171

X BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE, GUIDELINES AND LIMITATIONS 187

Introduction 187
Industry Category and Subcategory Covered 188
Identification of Best Available Technology Economically Achievable 188
Rationale for Selection of Best Available Technology Economically Achievable 188
Effluent Limitations Based on the Application of Best Available Technology Economically Achievable 190
Guidelines for the Application of Effluent Limitations 191

XI NEW SOURCE PERFORMANCE STANDARDS 193
Introduction 193
Industry Category and Subcategory Covered 194
Identification of Control and Treatment Technology Applicable to Performance Standards and Pretreatment Standards for New Sources 194
Rationale for Selection of Control and Treatment Technology Applicable to New Source Performance Standards 194
Standards of Performance Applicable to New Sources 195
Guidelines for the Applications of New Sources Performance Standards 196

XII ACKNOWLEDGEMENTS 197

XIII REFERENCES 199

XIV GLOSSARY 203

TABLES

Numbers		Page
1	Recommended Effluent Limitations for the Electroplating Industry to be Achieved by July 1, 1977, based on Best Practicable Control Technology Currently Available (BPCTCA)	4
2	Recommended Standards of Performance for the Electroplating Industry to be Achieved by New Sources	5
3	Process for Plating on Steel	15
4	Processes for Plating on Zinc Die Castings	16
5	Processes for Plating on Brass	17
6	Processes for Plating on Aluminum	18
7	Processes for Plating on Plastics	18
8	Distribution of Electroplate According to Type of Basis Material	20
9	Processing Sequences Decorative Copper Chromium Plating	22
10	Processing Sequences for Nickel Plating	23
11	Processing Sequences for Chromium Plating	23
12	Processing Sequences for Zinc Plating	24
13	Estimated Daily Raw Waste Load of Principal Salts Used in Copper, Nickel, Chromium, Zinc Plating and Related Processes	34
14	Principal Wastewater Constituents in Wastes From Processes for Plating on Steel	35
15	Principal Wastewater Constituents in Waste From Processes for Plating on Zinc Die Castings	36
16	Principal Wastewater Constituents in Waste From Processes for Plating on Brass	37
17	Principal Wastewater Constituents in	38

Waste From Processes for Plating on Aluminum

18 Principal Wastewater Constituents in Waste From Processes for Plating on Plastics 39

19 Approximate Concentrations of Waste Water Constituents Prior to Treatment From a Typical Facility Electroplating Copper, Nickel, Chromium, and Zinc (Plant 33-1) 51

20 Concentrations of Heavy Metals and Cyanide Achievable by Chemical Treating of Waste Created by Copper, Nickel, Chromium and Zinc Plating and Zinc Chromating Operations 74

21 Decomposition Products of Cyanide in Rinse Water From a Cyanide Zinc Electroplating Operation After Treatment with "Kastone" Peroxygen Compound 78

22 Estimated Costs for Small Electroplating Facilities With No Waste Treatment to Meet Effluent Limitations for 1977 and 1983 116

23 Geographical Distribution of Good Electroplating Waste Treatment Facilities Based on Initial Referrals, Companies Contacted for Information, and Representative Facilities Evaluated in Detail 129

24 Classification by Size, Type of Facility, and Effluent Discharge for 53 Electroplating facilities Selected for Evaluation 132

25 Classification of 53 Facilities Evaluated By Mix of Plating Operations and Type of Waste Treatment and In-Process Controls 134

26 Source of Information and Classification by Size and Waste Treatment Method 135

27 Size of Plating Operations 135

28 Treated Effluent Data 139

29 Comparison of Treated Effluent Data 146

Based on Total Amperage

30 Summary of Water Use Parameters for Four Plants Based on Copper, Nickel Chromium or Zinc Plating and Excluding Nonpertinent Metal Finishing Processes 159

31 Summary of Treated Effluent from Copper, Nickel, Chromium or Zinc Excluding Nonpertinent Plant Metal Finishing Operations 160

32 Summary of Treated Effluent Analysis During Second Round Visit for Comparison with Table 2 161

33 Compliance of Exemplary Plants with Tentative Effluent Limitations Guidelines 165

34 Monthly Average Effluent Concentration for Plant 33-1 Showing Improved Results Obtained Over a 14-Month Period 166

35 Comparison of Effluent Limitations for BPCTCA (Table 1) in Terms of Concentration for Various Effluent With the Prior Interim Guideline Concentrations 168

36 Typical Current Efficiencies Assumed forCalculationof Plated Area Using Equation (2) 175

37 English/Metric Unit Conversion 214

FIGURES

Number		Page
1.	Relationship of Total Metal in Treated Water Discharge to the Production Capacity of Typical Electroplating expressed as Metal Deposited Per Hour	26
2.	Schematic Flow Chart for Water Flow in Chromium Plating Zinc Die Castings Decorative	30
3.	Alternative Methods of Rinsing after a Processing Operation	31
4.	Diagram of a Typical Continuous-Treatment Plant	63
5.	Integrated Treatment System	65
6.	Batch Treatment of Cyanide Rinse Waters by the Kastone Process	79
7.	Schematic Presentation of Ion-Exchange Application for Plating-Effluent Treatment (7,25)	87
8.	Schematic Presentation of Ion-Exchange Operation at Plant 11-8	89
9.	Representative Closed-Loop System for Recovery of Chemicals and Water with a Single-Effect Evaporator	92
10.	Representative Open-Loop Evaporative Recovery System	94
11.	Closed-Loop System for Metal Finishing Process Water at Rock Island Arsenal	95
12.	Schematic Diagram of the Reverse-Osmosis Process for Treating Plating Effluents	97
13.	Schematic Diagram of Freezing Process for Recovery of Water and Chemicals from Plating Rinses (37,38)	101
14.	Schematic Diagram of Ion-Flotation Cell for Treatment of Plating Effluent	105
15.	Flow Chart for Treatment of Waste Water from Cleaner and Acid Dip When Plating Operations Have Separate Stream Treatment	110
16.	Effective of Size of Plating Plant on Investment	114

Cost of Waste-Treatment Facility

17. Cost Effectiveness of Treatments and In-Process Water Conservation Techniques 120

18. Employees Per Shift in Plating Versus Cumulative Percentage of 53 Plants 140

19. Total Installed Current for Plating Versus Cumulative Percentage of 53 Plants 141

20. Installed Rectifier Capacity in Amperes for Electroplating Versus Number of Employees Per Shift in Electroplating for 53 Plant Sample (Ration of Amperes Used To Amperes Installed is Typically 65 Percent) 142

21. Effluent Discharge Rate Versus Cumulative Percentage of 53 Plants 143

22. Composite of Pollutant Parameters in Treated Effluent Versus Cumulative Percentage of Plants 145

23. Water Use Based on Total Installed Current Versus Cumulative Percentage of 53 Plants 147

24. Comparison of the Water Use for Plants that use In-Process Chemical Recovery Systems on One or More Plating Operations with the Water Use of Plants that do not Use In-Process Recovery 149

25. Copper In Treated Effluent From Electroplating 150

26. Nickel In Treated Effluent From Electroplating 151

27. Hexavalent Chromium In Treated Effluent From Electroplating 152

28. Total Chromium In Treated Effluent From Electroplating 153

29. Zinc In Treated Effluent From Electroplating 154

30. Cyanide In Treated Effluent From Electroplating 155

31. Suspended Solids In Treated 156

Effluent From Electroplating

32. Typical Variation in Concentration of Pollutant Parameters From Analysis of Daily Composite Over a 4-Month Period Reported by Plant 11-8 162

33. Process Line for Example 1 179

34. Process Line for Example 2 181

35. Process line for Example 4 186

SECTION I

CONCLUSIONS

The electroplating of copper, nickel, chromium and zinc, on ferrous, nonferrous, and plastic materials is a single subcategory of the electroplating point source category for the purpose of establishing effluent limitations guidelines and standards of performance. The consideration of other factors such as the age of the plant, processes employed, geographical location, wastes generated and wastewater treatment and control techniques employed support this conclusion. The similarities of the wastes produced by electroplating operations and the control and treatment techniques available to reduce the discharge of pollutants further substantiate the treatment of copper, nickel, chromium and zinc electroplating as a single subcategory. However, guidelines for the application of the effluent limitations and standards of performance to specific facilities take into account the size of the electroplating facility and the mix of different electroplating processes possible in a single plant.

Presently, 13 of the 53 operating plants for which sufficient industry data were available achieve the concentrations of pollutants and water use estimate upon which the guidelines are based in the treated effluent using conventional chemical treatment systems. Of these 13 plants, 11 are captive and 2 are job shops. Verification testing on four of the plants show that two are meeting the guidelines. One is a captive and one is a job shop.

Only a small percentage of the raw waste generated by the electroplating industry is discharged directly to navigable waters without any treatment. The remainder of the industry can achieve the requirements as set forth herein with a minimum investment cost of $50,000 and a minimum operating cost of $13,000/year. For larger plants plating over 100 sq m/hr (1076 sq ft/hr) the operating cost will be less than 5 percent of the plating cost. The capital investment will be approximately $150,000 per 100 sq m/hr ($140,000 per 1000 sq ft/hr) of plated area. It is further estimated that no discharge of pollutants, when required, could be achieved with increased costs of about 10 percent of the total plating costs (including land and building). Capital investment will be approximately $100,000 to $200,000 per 100 sq m/hr (93,000 to $186,000 per 1000 sq ft/hr).

The development of data and recommendations in this document for effluent limitations guidelines and standards of performance for the electroplating industry (Phase I) relate to rack and barrel electroplating of copper, nickel, chromium, and zinc. This segment contributes about two-thirds of the total amount of chemicals added to wastewater in the electroplating industry.

SECTION II

RECOMMENDATIONS

Best Practicable Control Technology Currently Available

Recommended effluent limitations for the electroplating industry applicable to existing sources discharging to navigable waters are summarized in Table 1. The effluent limitations guidelines are based on the reduction of waste water pollutants and judicious water use. The reduction of waste water pollutants is achieved by chemical treatment of waste waters to destroy oxidizable cyanide, reduce chromium, and remove the metals to very low levels. Water consumption can be minimized by in-process control technology designed to recover and reuse process chemicals and water. The specific effluent limitations guidelines and rationale are discussed in greater detail in Section IX of this report.

Best Available Technology Economically Achievable

For the electroplating industry, no discharge of process waste water pollutants to navigable waters is recommended as the effluent limitation to be achieved by existing point sources by July 1, 1983. This represents the degree of effluent reduction believed to be attainable by existing point sources through the application of the Best Available Technology Economically Achievable. Section X of this report details the rationale of the effluent limitations guidelines for 1983.

New Source Performance Standards

Table 2 summarizes the recommended standards of performance for discharge to navigable waters applicable to new sources in the electroplating industry. In the case of electroplating, a new source is defined as an installation on which construction begins after publication of promulgated regulations prescribing a standard of performance.

The effluent limitations guidelines are based on the reduction of waste water pollutants and jucicious water use. The reduction of waste water pollutants is achieved by chemical treatment of waste waters to destroy oxidizable cyanide, reduce chromium, and remove to very low levels the metals. Water consumption can be minimized by in-process control technology designed to recover and reuse process chemicals and water. Section XI details the reationale for the effluent limitations guidelines for new sources.

Preceding page blank

TABLE 1. RECOMMENDED EFFLUENT LIMITATIONS FOR THE ELECTROPLATING INDUSTRY TO BE ACHIEVED BY JULY 1, 1977, BASED ON BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE (BPCTCA)

Parameter	Effluent Limitations (a)			
	Single Day Maximum (b)		30-Day Average (c)	
	mg/sq m/op	lb/10^6 sq ft/op	mg/sq m/op	lb/10^6 sq ft/op
Copper (Cu) (d)	160	32.7	80	16.4
Nickel (Ni) (d)	160	32.7	80	16.4
Chromium hexavalent (Cr^{6+}) (d)	16	3.3	8	1.6
Chromium, total (Cr_T) (d) (e)	160	32.7	80	16.4
Zinc (Zn) (d)	160	32.7	80	16.4
Cyanide, oxidizable (CN) (f)	16	3.3	8	1.6
Cyanide, total (CN) (g)	160	32.7	80	16.4
Total Suspended Solids (TSS) (h)	4800	982	3200	654
pH range 6 to 9.5 (i)				

See Footnotes on page 6

TABLE 2 . RECOMMENDED STANDARDS OF PERFORMANCE FOR THE ELECTROPLATING INDUSTRY TO BE ACHIEVED BY NEW SOURCES

Parameter	Standards of Performance(a)			
	Single Day Maximum(b)		30-Day Average (c)	
	mg/sq m/op	lb/10^6 sq ft/op	mg/sq m/op	lb/10^6 sq ft/op
Copper (Cu) (d)	80	16.4	40	8.2
Nickel (Ni) (d)	80	16.4	40	8.2
Chromium, hexavalent (Cr^{6+}) (d)(e)	8	1.6	40	0.8
Chromium, total (Cr_T) (d) (e)	80	16.4	40	8.2
Zinc (Zn)(d)	80	16.4	40	8.2
Cyanide, oxidizable (CN) (f)	8	1.6	4	0.8
Cyanide, total (CN) (g)	80	16.4	40	8.2
Total Suspended Solids (TSS) (h)	2400	491	1600	327
pH range 6 to 9.5 (i)				

See Footnotes on page 6

FOOTNOTES FOR TABLES 1 and 2

(a) The effluent limitations and standards of performance are defined as the weight of pollutant in milligrams discharged per square meter per operation. An operation is defined as any step in the plating process in which copper, chromium, or zinc metal or chromate is deposited on a base material followed by a rinse.

(b) Single Day Maximum is the maximum value for any one day

(c) 30-Day Average is the maximum average of daily values for any consecutive 30 days

(d) Total metal (soluble and insoluble) in sample.

(e) Total chromium (Cr_T) is the sum of all ionic forms (Cr^{+3} + Cr^{+6}).

(f) Oxidizable cyanide is defined as detectable cyanide amenable to oxidation by chlorine according to stanard analytical procedures.

(g) Total cyanide is defined as all detectable cyanide in the sample following distillation according to standard analytical procedures.

(h) Total suspended solids retained by a 0.45 micron filter according to standard analytical procedures.

(i) A pH in the range of 8 to 9 is the best range for minimizing the soluble metal-concentation during coprecipitation, as discussed in Section VII.

SECTION III

INTRODUCTION

Purpose and Authority

Section 301(b) of the Act requires the achievement by not later than July 1, 1977, of effluent limitations for point sources, other than publicly-owned treatment works, which are based on the application of the best practicable control technology currently available as defined by the Administrator pursuant to Section 304(b) of the Act. Section 301(b) also requires the achievement by not later than July 1, 1983, of effluent limitations for point sources, other than publicly-owned treatment works, which are based on the application of the best available technology economically achievable which will result in reasonable further progress toward the national goal of eliminating the discharge of all pollutants, as determined in accordance with regulations issued by the Administrator pursuant to Section 304(b) to the Act. Section 306 of the Act requires the achievement by new sources of a Federal standard of performance providing for the control of the discharge of pollutants which reflects the greatest degree of effluent reduction which the Administrator determines to be achievable through the application of the best available demonstrated control technology, processes, operating methods, or other alternatives, including where practicable, a standard permitting no discharge of pollutants.

Section 304(b) of the Act requires the Administrator to publish within one year of enactment of the Act, regulations providing guidelines for effluent limitations setting forth the degree of effluent reduction attainable through the application of the best practicable control technology currently available and the degree of effluent reduction attainable through the application of the best control measures and practices achievable including treatment techniques, process and procedure innovations, operation methods and other alternatives. The regulations proposed herein set forth effluent limitations guidelines pursuant to Section 304(b) of the Act for the electroplating point source category.

Section 306 of the Act requires the Administrator, within one year after a category of sources is included in a list published pursuant to Section 306(b)(1)(A) of the Act, to propose regulations establishing Federal standards of performances for new sources within such categories. The Administrator published in the Federal Register of January 16, 1973 (38 FR 1624), a list of 27 source categories.

Publication of the list constituted announcement of the Administrator's intention of establishing, under Section 306, standards of performance applicable to new sources within the electroplating subcategory of the metal finishing industry which was included within the list published January 16, 1973.

Summary of Methods Used for Development of the Effluent Limitation Guidelines and Standards of Performance

The effluent limitations guidelines and standards of performance recommended herein were developed in the following manner. The point source subcategory of electroplating was first examined to determine whether separate limitations and standards would be appropriate for different segments. Such subcategorization was based upon raw material used, product design, type of basis material, size and age of facility, number of employees, geographic location, quantity of work processed, waste characteristics, treatability of wastes, and rack plating versus barrel plating. The raw-waste characteristics for each subcategory were then identified. This included an analyses of (1) the source and volume of water used in a process and the sources of waste and waste waters in representative plants; and (2) the constituents of all waste waters including those which are potentially harmful and result in taste, odor, and color in water or aquatic organisms. The constitutents of waste waters which should be subject to effluent limitations guidelines and standards of performance were then identified.

The full range of control and treatment technologies along with their problems, limitations, and reliability, cost and energy requirements were identified. This included in-plant and end-of-process technologies, which are existent or capable of being designed for each subcategory. The quantity and the chemical, physical, and biological characteristics of each pollutant were identified along with the reduction associated with the application of each of the treatment and control technologies. The environmental impacts on non-water quality aspects such as air, solid waste, and noise were also investigated.

The information, was then evaluated to determine what levels of technology constituted the "best practicable control technology currently available," "best available technology economically achievable" and the "best available demonstrated control technology, processes, operating methods, or other alternatives." In identifying such technologies, various factors were considered. These included the total cost of application of the technology in relation to the effluent reduction benefits to be achieved from such application, the age of equipment and facilities involved, the process employed, the engineering aspects of the application of various types of control techniques process changes, nonwater quality environmental impact (including energy requirements) and other factors.

Companies plating copper, nickel, chromium and zinc and reporting low levels of pollutants in their waste discharge to EPA regional offices or state authorities were contacted by telephone or letter to develop quantitative data on volume of production (or direct current use), water flow rate and composition of waste water discharge. This list of companies was supplemented by others suggested by trade associations and several suppliers of waste treatment equipment. From the information collected from more than 200 companies, data on plants having a volume of effluent flow or discharge of pollutants that reflected inferior treatment technology were excluded from the analysis of pollutant reductions achievable by the application of the best practical control technology. Data from 53 companies practicing good waste treatment were expanded by 23 plant visits and analyzed to identify the control and treatment technologies which became the basis for the effluent limitations and standards of performance recommended in Section II. This group of 53 companies included 12 independent job shops employing from 16 to 200 workers. Size in terms of installed current capacity ranged from 6,000 to 263,000 amperes among the independent shops and 3,000 to 450,000 amperes among the captive facilities. Chemical waste treatment was practiced by all but two companies, which used evaporators to recycle plating rinse water; 13 companies utilized integrated chemical treatment; 13 employed evaporators to reduce the water flow rate from one, two or three plating processees. Four utilized ion exchange units and two used reverse osmosis for some plating processes. Two companies were using counterflow rinses for reclaiming plating solution dragged into rinse water. A total of 21 companies employed batch or continuous chemical treatment exclusively.

Information Sources

Sources of information utilized for developing the data in this document included the following:

(1) Published literature (References appear in Section XIII)
(2) Trade literature
(3) Technology Transfer Program on Upgrading Metal Finishing Facilities to Reduce Pollution, December 12-13, 1972, sponsored by Environmental Pollution Agency
(4) Pollution Abatement Seminar, sponsored by the Metal Finishing Suppliers Association, January 23, 1973, Cleveland, Ohio
(5) Ten EPA regional offices and 32 state pollution abatement offices
(6) Representatives of the American Electroplaters' Society, (AES), the Metal Finishing Suppliers' Association (MFSA) and the National Association of Metal Finishers (NAMF)
(7) Representatives of 130 companies with facilities for electroplating copper, nickel, chromium, or zinc, during telephone conferences
(8) Representatives of seven companies during office conferences
(9) Representatives of 23 companies were visited by BCL staff members for development of detailed data
(10) Analytical verification of effluent data for five plants engaged in electroplating copper, nickel, zinc, and/or chromium. These five companies included captive facilities and job shops.

General Description of the Electroplating Industry

The electroplating industry, a subcategory of the metal finishing activities included in standard industrial classification (SIC) 3471, is defined for the purpose of this document as that segment of industry applying metallic coatings on surfaces by electrodeposition and includes both independent (job) platers and captive operations associated with product fabrication and assembly. The annual dollars-added value by electroplating exceeds $2,000,000,000. Approximately 20,000 companies are engaged in metal finishing, approximately 3500 of these are shops supplying only plating service. About 25 percent of this segment is concentrated in the middle western states of Illinois, Michigan, and Ohio. Another 20 percent is concentrated in eastern Pennsylvania and the Atlantic coastline states of Connecticut, Rhose Island, New York and New Jersey. The location of captive plating facilities follows the same general pattern.

The energy consumed annually by electroplating is estimated to be in the range of 1 to 1.5×10^9 kilowatt hours. From 9×10^7 to 1×10^8 kg (100,000 to 120,000 tons) of metal (principally copper, nickel, zinc, and tin) is converted annually to electroplated coatings. These coatings provide corrosion protection, wear or erosion resistance, antifrictional characteristics, lubricity, electrical conductivity, heat and light reflectivity or other special surface characteristics, which enables industry to conserve several millions of tons of critical metals, such as: cobalt, chromium, nickel, silver and gold. Electroplated coating thickness usually ranges from 0.0006 to 0.004 cm (0.00025 to 0.0015 inch), but thicker coatings to 0.025 or 0.04 cm (0.010 to 0.015 in.) are sometimes required for special engineering purposes or for salvaging worn or mismachined parts.

An electroplating process includes cleaning, electroplating, rinsing and drying. The cleaning operation consists of two or more steps that are required for removing grease, oil, soil, and oxide films from the basic metal surface and insuring good electroplate adhesion. Sequential treatments in an alkaline solution and an acid solution with intermediate rinsing are the minimum number customary for these purposes. In the electroplating solution, metal ions in either acid, alkaline or neutral solutions are reduced on cathode surfaces, which are the work pieces being plated. The metal ions in solution are usually replenished by the dissolution of metal from anodes in bar form or in small pieces contained in inert wire or expanded metal baskets, but replenishment with metal salts is sometimes practiced, especially for chromium plating. In this case, an inert material must be selected for the anodes. Hundreds of different electroplating solutions have been adopted commerically, but only two or three types are utilized widely for a single metal or alloy. Cyanide solutions are popular for copper, zinc, and cadmium, for example, yet non-cyanide alkaline solutions containing pyrophosphate or another chelating agent have been adopted recently for zinc and copper. Acid sulfate solutions also are used for zinc, copper, and several other metals, especially for plating relatively simple shapes.

Barrels are used for small parts that tumble freely in rotating barrels. Racks are to be used for larger parts that cannot be tumbled without surface impingment. Perforated plastic barrels range in diameter from 15 to 75 cm (6 to 30 in.), depending on part size and shape. Direct current loads up to several hundred amperes are distributed to the parts being plated in horizontal barrels through danglers suspended from a current carrying bar located at the longitudinal axis. In oblique barrels, a conductive button at the bottom transmits the current.

Rack plating is required for perhaps 90 percent of the surface area processed commercially; the parts are attached to plastic-coated copper frames designed to carry current equitably to a few hundred small parts, several medium-sized shapes or just a few large products through spring-like rack tips affixed to the rack spines. Racks fabricated for manual transfer from cleaning, plating and rinsing tanks usually contain 2 to 7 kg (5 to 15 pounds) of parts having a surface area of 0.5 to 1 sq meter (5 to 10 sq ft). Larger racks for holding heavier parts are constructed for use with mechanical hoist and transfer systems. Mechanized transfer systems for both barrels and racks, which range in cost from $50,000 to more than $1,000,000 are being utilized for high-volume production involving six to thirty sequential operations. In some instances, dwell time and transfer periods are programmed on magnetic tape or cards for complete automation.

Electroplating facilities vary greatly in size and character from one plant to another. The size of a single facility expressed as plating solution volume ranges from less than 400 liters (100 gallons) to more than 190,000 liters (50,000 gallons). The area of the products being electroplated in these facilities varies from less than 10 to more than 1000 sq meters/day (100 to 10,000 sq ft/day). The power consumed by a single facility varies from a few kilowatt hours/day to as much as 20,000 kilowatt-hours/day. Products being plated vary in size from less than 6.5 sq cm (1 sq in.) to more than 1 sq meter (10 sq ft) and in weight from less than 30 g (1 oz) to more than 9000 kg (10 tons). Continuous strip and wire are plated in some plants on a 24-hour/day basis.

Some companies have capabilities for electroplating ten or twelve different metals and alloys, but other specialize in just one or two. Because of differences in character, size and processes, few similar plants exist at the present time. Construction of facilities has been tailored to the specific needs of each individual plant, but the technologies used are the same across the industry.

SECTION IV

INDUSTRY CATEGORIZATION

Introduction

This section discusses in detail the scope of the metal finishing industry. The rationale is developed for considering the electroplating industry as a separate subcategory for the development of effluent limitations guidelines and standards of performance. Further rationale is offered for the selection of copper, nickel, chromium, and zinc electroplating for study in Phase I and all other metal electroplating in Phase II. The rationale is then developed to show why further subcategorization of the electroplating industry is not required for the purpose of developing effluent limitation guidelines and standards of performance.

Objectives of Categorization

A primary purpose of industry categorization is to develop quantitative effluent limitations and standards of performance that are uniformly applicable to a specific category or subcategory. This does not preclude further classification within a category for the purpose of monitoring to insure compliance.

The Relationship of Electroplating and Metal Finishing

Electroplating is one of several processes in the broader category of metal finishing, which includes anodizing, bright dipping, buffing, coloring, conversion coating, descaling, electropolishing, galvanizing, mechanical polishing, tumbling, and other finishing processes. One, several, or all of the above processes may be performed in a single facility.

Profile of Production Processes

The electroplating industry utilizes chemical and electrochemical operations to effect an improvement in the surface properties of metals and other materials.

In one segment of the industry, identified as No. 3471 in the Standard Industrial Classification (SIC) Manual 1972, published by the Executive Office of the President (Bureau of the Budget), processes are performed on metals or other materials as products owned by a second party. Such work is done in job shops, also known as contract shops. The same operations for electroplating are performed by manufacturers classified by other SIC numbers, on their own metals, materials, and products in captive shops under their own management. Typical processes are the same for

Preceding page blank

both types of facilities. Examples are shown for copper, nickel, chromium, and zinc plating which is the subject of this report according to basis metal or material and operations in Tables 3 to 7. Not shown in these tables are sequences for electroplating cadmium, brass, gold, iron, lead, silver, tin, the platinum metals, and other metals and alloys which are practiced by only a few companies, relative to the much larger number engaged in electroplating copper, nickel, chromium, and zinc. These less common electroplating processes will be examined and analyzed later during Phase II of this program. Copper, nickel, chromium, and zinc plating processes which is the subject of this report were selected first, because a large proportion (about two thirds) of the waste generated by electroplating processes are derived from those associated with copper, nickel, chromium, and zinc. Furthermore, almost all facilities are equipped for plating at least one of these common metals.

An electroplating process includes a succession of operations starting with cleaning in alkaline solutions, acid dipping to neutralize or acidify the wet surface of the parts, followed by the steps of electroplating, copper, nickel, chromium, or zinc. These operating solutions are the sources of pollutants which appear in the rinses immediately following the concentrated solutions, in spills, and from the discard of spent or contaminated solutions. The intermediate rinses are essential for removing the processing solution from the workpieces so as to avoid contaminating the next processing solution. The final rinse assures a clean finished surface.

Some generalizations will be encountered as process descriptions. For example, decorative chromium plating refers to copper plus nickel plus chromium plating and hard chromium plating refers to only chromium (usually on steel), as seen in Table 3.

In some facilities, vapor degreasing with tri- or perchloroethylene precedes the alkaline cleaner. The only water associated with this operation is for cooling. The cooling water effluent is usable for rinsing after the alkaline cleaning. Therefore, no further mention is made of vapor degreasing. However, it is a source of possible air pollution.

For each typical electroplating operation, exemplified in Tables 3 to 8, a variety of solutions can be selected. The choice is usually based on personal knowledge and experience in a specific process for a specific basis material. The selection of an alkaline cleaner for a specific basis material could be made from at least five types.

Further evidence of the complex character of the electroplating industry is seen in the size range of less than 400 liters (100 gallons) to more than 190,000 liters (50,000 gallons) of plating solutions in a single facility. The less than 400 liter (100 gallon) installations involve parts either small in size or

TABLE 3. PROCESSES FOR PLATING ON STEEL

	Decorative Chromium Plating 1	Decorative Chromium Plating 2	Hard Chromium Plating 3	Copper Cladding 4	Protective Zinc Plating 5	Protective Zinc Plating 6	Carburizing Resist 7	Protective Nickel Plating 8
Alkaline clean/ rinse	X	X	X	X	X	X	X	X
Acid dip/rinse	X	X	X	X	X	X	X	X
Copper strike/ rinse	X			X				
Acid dip/rinse	X			X				
Copper/rinse	X			X			X	
Semibright nickel/ rinse	X	X						X
Bright nickel/ rinse	X	X						
Anodic treat/ rinse			X					
Chromium/rinse	X	X	X					
Zinc rinse					X	X		
Chromate/rinse						X		

TABLE 4 PROCESSES FOR PLATING ON ZINC DIE CASTINGS

Operation	Decorative Chromium Plate 1	Decorative Chromium Plate 2	Protective Finish 3	Protective Finish 4
Alkaline clean/ rinse	X	X	X	X
Acid dip/rinse	X	X	X	X
Copper strike/ rinse	X	X		
Acid dip/rinse		X		
Copper/rinse	X	X		
Nickel/rinse	X	X		
Nickel/rinse	X	X		
Anodic treat/ rinse			X	
Chromium/rinse	X	X		
Chromate/rinse				X

TABLE 5. PROCESSES FOR PLATING ON BRASS

Operation	Chromium Plate 1	Decorative Chromium Plate 2	Decorative Chromium Plate 3	Protective Nickel Plate 4
Alkaline clean/ rinse	X	X	X	X
Acid dip/rinse	X	X	X	X
Copper strike/ rinse	X	X	X	X
Acid dip/rinse				X
Copper/rinse				
Nickel/rinse	X	X	X	X
Nickel/rinse			X	
Anodic treat/ rinse				
Chromium/rinse	X	X	X	

TABLE 6 PROCESSES FOR PLATING ON ALUMINUM

Operation	Decorative Chromium Plate 1	Decorative Chromium Plate 2	Decorative Chromium Plate 3	Protective Zinc Plate 4
Alkaline Clean/rinse	X	X	X	X
Acid dip/rinse	X	X	X	X
Activate/rinse	X	X	X	X
Zinc strike/rinse	X	X		X
Copper strike/rinse	X	X		
Copper/rinse	X	X		
Nickel/rinse	X	X		
Nickel/rinse		X		
Chromium/rinse	X	X	X	
Zinc/rinse				X
Chromate/rinse				X

TABLE 7 PROCESSES FOR PLATING ON PLASTICS

Operation	Decorative Chromium Plate 1	Decorative Chromium Plate 2	Basis for Coating 3	Basis for Magnetic Coating 4
Alkaline Clean/rinse	X	X	X	X
Acid dip rinse	X	X	X	X
Activate rinse	X	X	X	X
Catalyze rinse	X	X	X	X
Electroless Deposit/rinse	X	X	X	X
Copper strike/rinse	X			
Copper/rinse	X	X	X	
Nickel/rinse	X	X	X	X
Nickel/rinse		X		
Chromium/rinse	X	X		

quantity or specialized such electrodepositing chromium on tools and custom parts in a captive shop. Installations of larger volumes process parts large in size such as bumpers for automobiles, sheet and strip steel for prefab plating and/or large numbers of zinc die castings and steel and brass stampings or castings.

At the low and intermediate region of the size range are the contract shops, representing approximately 3500 facilities of SIC 3471 classification. Larger facilities are in captive shops where logistics and process control are more effectively geared to a high production volume. Other SIC classification numbers cover the captive plating facilities, estimated to be five to six times the number of contract or job shops. About 90 percent of the volume of electroplating in dollars-added value is supplied by companies doing their own electroplating on their own products.

Unlike most of the captive plating operations, which process approximately the same number of the same products each month, job shops are required to handle a greater variety of shapes and different metal substrates. Production volume for a specific type of product varies appreciably from day to day. Thus, an individual job shop might be generating a large amount of copper, nickel, and chromium waste and little or no zinc waste during a limited, three- or four-week period at the beginning of a new model-year season for automotive or appliance hardware, or a much lesser amount of copper, nickel, and chromium waste and a large amount of zinc waste near the end of a model-year run for typical customer products. Day-to-day variations can be expected in the amount and type of waste generated by a typical independent facility as a result of meeting agreed on delivery schedules.

Because of the large variety of products handled by the independent job shops, in-process controls for minimizing waste are less effective, in comparison with the controls that can be exercised in a captive facility always processing the same products and materials. As a result of this situation, the advent of rigid waste-discharge enforcement is expected to encourage some degree of specialization among the independent job-shop establishments. Such a trend will reverse the tendency established in the past by companies that have expanded in facilities with a larger number of electroplating and finishing processes in order to provide improved service to industry in a given geographical area.

Materials Receiving Electroplates

Regardless of the size of facility for copper, nickel, chromium, and/or zinc electroplating, it will process one or more of the commonly used basis materials: steel, zinc die castings, brass, aluminum, and plastic such as ABS and polypropylene as summarized in Tables 3 to 7. The distribution of electroplating according to basis material is shown in Table 8. More than half of all electroplating is done on steel as a basis material. Zinc alloys as die castings comprise the next largest category of basis materials. Reference to Tables 3 to 6 shows that basis materials are first cleaned and acid dipped prior to the first electroplating step.

TABLE 8. DISTRIBUTION OF ELECTROPLATE ACCORDING TO TYPE OF BASIS MATERIAL

	Percent by Basis Material				
Plate	Steel	Zinc Die Cast	Brass	Aluminum	Plastics
Copper	50	46	2		2
Nickel	48	44.9	5	0.1	2
Chromium	54	33.9	4	0.1	2
Zinc	100				

Factors Considered in Categorization

When the nature of the industry and the operations performed were analyzed, consideration was given to the further categorization of electroplating according to one or more of the following:

(1) Type of basis material
(2) Product design
(3) Raw materials used
(4) Size and age of facility
(5) Number of employees
(6) Geographic location
(7) Quantity of work processed
(8) Waste characteristics
(9) Treatability of wastes
(10) Rack plating versus barrel plating.

Type of Basis Material

The wastes produced by processing all common basis materials are similar. A single facility can process all basis materials without significant change in the raw materials consumed or the waste-treatment technique adopted for control of end-of-pipe water discharge. Although it is possible that the basis material may contribute to the waste stream when alkaline cleaned and acid dipped, it is an insignificant quantity when compared to the waste generated from the plating solutions by the rinsing of the plated object. Any materials dissolved from the surface of the customary basis metals during processing are removed from wastewater discharge by the treatment processes adopted for removing copper, nickel, chromium and zinc, which are described in Section VII. Furthermore, the basis materials selected for most consumer products frequently are interchanged from one model year to another. Therefore, the type of basis material does not constitute a basis for subcategorization.

Product Design

Although complex shapes tend to generate more waste than simpler ones, the premium in costs for fabricating and plating the complex shapes far overshadows any small supplemental waste-treatment cost for such products. Product design precepts for minimizing electroplating costs also reduce wastes created by electroplating processes (1). Furthermore, the in-process controls and rinsing techniques described in Section VII for minimizing the wastes generated by copper, nickel, chromium, and zinc electroplating processes have been adopted for canceling the effect of the shape factor. Therefore, product design variance is not a basis for subcategorization.

Raw Materials Used

Raw materials do not provide a basis for subcategorization, because practicable waste-treatment technology identified in Section VII is equally applicable to all of the usual procedures and solutions described previously for electroplating copper, nickel, chromium, and zinc. In any facility carrying out one or more of the processes shown in Tables 3 to 12, the same waste-treatment needs arise. Such variations as exist for each operation are not unique and do not affect the waste-treatment technology and control.

TABLE 7 PROCESSING SEQUENCES DECORATIVE COPPER-NICKEL-CHROMIUM PLATING

Required Process	Steels			Cast Iron	Copper and Copper Base Alloys	Zinc Die Castings	Aluminum and Its Alloys	Nickel and Its Alloys
	Low Carbon	High Carbon*	Stainless					
(1) Oil and grease removal	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease
(2) Scale removal	Acid pickle rinse	Anodic pickle rinse	HNO_3/HF rinse	Mechanical or anodic pickle rinse	Acid or cyanide dip rinse	Mechanical rinse	Bright dip rinse	Pickle rinse
(3) Pretreatment	Soak clean rinse	Soak clean rinse	Electropolish rinse	Soak clean rinse	Cathodic or anodic rinse	Cathodic or anodic rinse	Soak clean rinse	Cathodic clean anodic clean rinse
	Anodic clean rinse Acid dip rinse	Anodic clean rinse Etch rinse	Anodic clean rinse	Cathodic clean rinse Anodic acid rinse	Acid or cyanide dip rinse	Acid dip rinse	Acid dip rinse	Cyanide dip rinse Acid dip rinse
		Anodic clean or NaCN-dip rinse Acid dip rinse						
(4) Preplate	Copper strike rinse	Copper strike rinse	Activate anodic cathodic	--	--	Copper strike	Zinc immersion rinse	Activate anodic cathodic
							Zinc immersion rinse Copper strike	
(5) Copper plate	Cyanide copper rinse or acid dip rinse	Cyanide copper rinse or acid dip rinse	--	Cyanide copper rinse or acid dip rinse	Cyanide copper rinse	Cyanide copper rinse Acid dip rinse	Cyanide copper rinse Acid dip rinse	--
	Acid copper rinse	Acid copper rinse		Acid copper rinse		Acid copper rinse	Acid copper rinse	
(6) Nickel plate	Acid dip after cyanide copper rinse Semibright nickel Bright nickel rinse	} for all basic metals						
(7) Chromium plate	Chromium plate rinse Hot rinse	} for all basic metals						

* Also base alloy steels.

TABLE 10 PROCESSING SEQUENCES FOR NICKEL PLATING

Required Process	Steels: Low Carbon	Steels: High Carbon	Steels: Stainless	Cast Iron	Copper and Its Alloys	Zinc Die Castings	Aluminum and Its Alloys	Nickel and Its Alloys
(1) Oil and grease removal	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease
(2) Scale removal	Acid pickle rinse	Anodic pickle rinse	HNO_3/HF rinse	Mechanical or anodic pickle rinse	Acid or cyanide rinse	Mechanical	Bright dip rinse	Pickle rinse
(3) Pretreatment								
(4) Preplate	Nickel strike	Nickel strike	Activate anodic cathodic	Nickel strike	--	Cu-strike Cyanide copper rinse Acid dip rinse Acid copper rinse	Cu-strike rinse Acid dip rinse	Nickel strike
(5) Nickel plate	Watts nickel Semibright nickel Bright nickel Any one or any combination thereof	} for all base metals						

TABLE 11 PROCESSING SEQUENCES FOR CHROMIUM PLATING

Required Process	Steels: Low Carbon	Steels: High Carbon	Steels: Stainless	Cast Iron	Copper and Its Alloys	Zinc Die Castings	Aluminum and Its Alloys	Nickel and Its Alloys
(1) Oil and grease removal	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease	Degrease
(2) Scale removal	Acid pickle rinse	Anodic pickle rinse	HNO_3/HF rinse	Mechanical or anodic pickle rinse	Acid or cyanide dip rinse	Mechanical rinse	Bright dip rinse	Pickle rinse
(3) Pretreatment	Anodic clean rinse	Anodic clean rinse	Soak clean rinse	Anodic clean rinse	Cathodic clean Anodic clean rinse	Sequence "A" only	Soak clean rinse	Sequence "A"
	Anodic chromic acid --	Anodic chromic acid --	Anodic clean rinse Acid dip rinse or anodic in chromic acid	Anodic in chromic acid	Acid dip rinse		Cathodic etch rinse Acid dip rinse or sequence "A"	
(4) Preplate	--	--	--	Chrome flash	--		Copper	Copper or nickel
(5) Plate	Hard chromium rinse Hot rinse	Hard chromium rinse Hot rinse	Decorative or hard chromium rinse Hot rinse	Hard chromium rinse Hot rinse	Decorative chromium rinse Hot rinse	Decorative chromium rinse Hot rinse	Decorative chromium rinse Hot rinse	Decorative chrome rinse Hot rinse

TABLE 12 PROCESSING SEQUENCES FOR ZINC PLATING

Required Process	Steels		Cast Iron	Copper and Its Alloys	Aluminum and Its Alloys
	Low Carbon	High Carbon			
(1) Oil and grease removal	Degrease	Degrease	Degrease	Degrease	Degrease
(2) Scale removal	Acid pickle rinse	Anodic pickle rinse	Mechanical or anodic pickle rinse	Acid or cyanide dip rinse	Bright dip rinse
(3) Pretreatment	Soak clean rinse Anodic clean rinse Cyanide dip rinse	Soak clean Cathodic clean rinse Acid dip or anodic acid rinse	Soak clean Cathodic clean rinse Acid dip or anodic acid rinse	Sequence "A"	Sequence "A"
(4) Preplate	--	Copper strike or acid zinc strike rinse	Copper strike or acid zinc strike rinse	Copper strike rinse*	
(5) Plate	High cyanide zinc or low cyanide zinc or acid zinc or zinc fluoborate rinse	} for all base metals			
(6) Posttreatment	Acid bright dips Acid rinse Chromate conversion coatings rinse Hot rinse	} for all base metals			

* For soldered parts only.

Size and Age of Facility

The nature of electroplating is the same in all facilities regardless of size and age. For example, copper plating is technically the same in 190 liters (50 gallons) as in 19,000 liters (5,000 gallons) or larger installations. Technically, the age of the facility does not alter this situation. Electroplating of nickel, chromium, and zinc follows the same pattern. Thus, the characteristics of the waste will be the same for plants of all ages and sizes. Only the quantity of waste per unit time will differ. Yet, this factor is not a basis for subcategorization, because waste discharge after treatment is directly proportional to the size of the facility expressed as amount of metal deposited, as shown in Figure 1. The amount of metal deposited in typical facilities is directly related to the current consumed for plating, the number of liters of installed plating solution, and the volume of production. The guidelines recommended in this document provide for variable production volume with no need to differentiate plant capacity as a subcategory.

It is recognized that some small plating facilities may have insufficient space for accommodating effective in-process controls for minimizing water use and/or conventional chemical waste treatment equipment. The capital investment/burden for installing good waste control may be greater for such small companies relative to the burden that can be amortized by larger companies. In such cases, heavy metal pollutants can be absorbed on the resins in small ion-exchange units available at relatively modest investment. At least one vendor of such equipment will replace the resin beds, back wash the used beds in their own facilities and regenerate the resins for reuse. Alternatively, both local and regional organizations equipped with large tank trucks supply a hauling and treating service in several areas. It is also possible that a small electrodialysis system would provide recycling of cyanide. Costs depend on water volume and the concentration of pollutants. However, because of economic reasons, shops plating less than 33 sq m/hr or having an installed current capacity of less than 2000 amperes are required only to destroy the cyanide, equalize and pH adjust their waste prior to discharge.

Number of Employees

The number of employees engaged in electroplating does not provide a basis for subcategorization, because electroplating operations can be carried out manually or in automatic machines which greatly conserve labor. For example, an operation with 3,785-liter (1,000-gallon) processing tanks may require six people if operated manually, whereas a plant of the same tank size and carrying out the same operations in an automatic machine would need only two people. The same amount of waste would be generated in each case, if the products being plated were equal in total area. Other examples could be cited to show that no basis exists for relating the number of employees to the

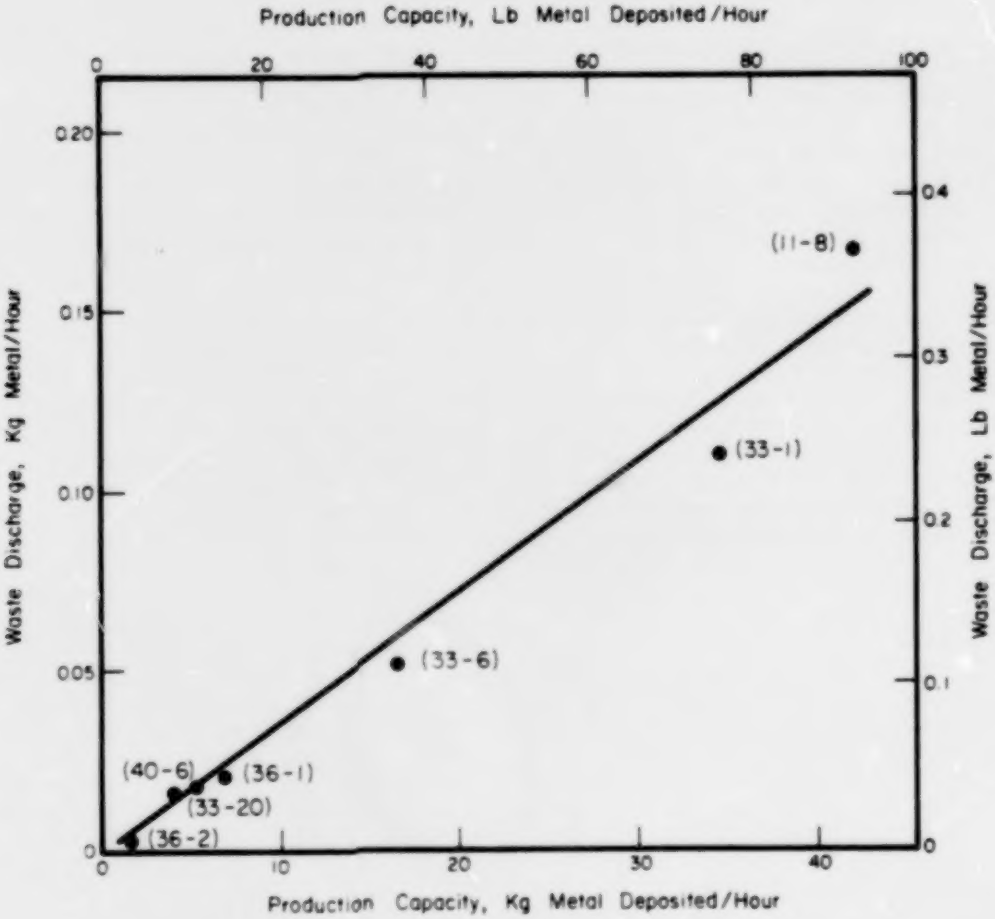


FIGURE 1. RELATIONSHIP OF TOTAL METAL IN TREATED WATER DISCHARGE TO THE PRODUCTION CAPACITY OF TYPICAL ELECTROPLATING PLANTS EXPRESSED AS METAL DEPOSITED PER HOUR

electroplating operations carried out and/or to the waste that results from those operations.

Geographic Location

Geographic location is not a basis for subcategorization. No condition is known whereby the choice of electroplating operations is affected by the physical location of the facility, except availability of process water. If water is not available, no modification of electroplating procedures can compensate for this lack. No electroplating facilities would be installed at a water-deficient location, because large amounts of water are required for replacing water lost by evaporation. The waste-treatment procedures described in Section VII can be utilized in any geographical area. In the event of a limitation in the availability of land space for constructing a waste-treatment facility, the in-process controls and rinsewater conservation techniques described in Section VII can be adopted for minimizing the land space required for the end-of-process treating facility. A compact unit can easily handle end-of-process waste if the best in-process techniques are utilized to conserve raw materials and/or water consumption.

Quantity of Work Processed

Quantity of work processed is analogous to plant size. Therefore, the discussion about plant size is equally applicable to the quantity of work processed. The application of the guidelines provides for the production of a particular facility.

Waste Characteristics

The physical and chemical characteristics of all wastes generated by copper, nickel, chromium, and zinc electroplating processes are similar. Specifically, all wastes are amenable to the conventional waste-treatment technology detailed in Section VII. The characteristics of treated waste are the same througout the industry. Thus waste characteristics do not constitute a basis for subcategorization.

Treatability of Wastes

As no peculiarity exists between raw materials and waste characteristics as a basis to separate facilities into subcategories, none exists for treatability of wastes as a basis for subcategorization. All of the principal treatment procedures and in-process controls are technically applicable by choice for any given waste and all operations generate the same type of raw waste regardless of the facility.

Rack Plating Versus Barrel Plating

The choice of rack or barrel methods for plating is based on the size and quantity of the parts to be processed per unit of time. Neither of these conditions imposes a significant technical change in the operations for electroplating. The selection is always based on economic considerations because hand racking of small parts is usually more costly than barrel processing in bulk. Sometimes plating bath compositions will be modified by altering the concentration of solution constituents. However, the same types of salts, acids, and additives will be used. Thus, the impact on waste characteristics is not changed. The volume of wastewater (dragout) is frequently greater in barrel plating operations but the final effluent quality is not a function of influent concentration. Techniques are available to reduce the rinse water volumes in barrel plating to the levels of rack plating. These techniques are detailed in Section VII. Therefore, rack plating and barrel plating are not appropriate subcategories.

SECTION V

WASTE CHARACTERIZATION

Introduction

Water flow and the sources, nature and quantity of the wastes dissolved in the water during copper, nickel, chromium, and zinc plating processes are described in this section. Water is a major material in the electroplating industry and is associated with every operation. Yet, none of the water enters the product.

Specific Water Uses

Water is used in the following ways:

(1) Rinsing to remove films of processing solution from the surface of work pieces at the site of each operation
(2) Washing away spills in the areas of the operations
(3) Washing the air that passes through ventilation ducts so as to remove spray from the air before it is exhausted
(4) Dumps of operating solutions, mostly pretreatment and posttreatment solutions
(5) Rinse water and dumps of solutions from auxiliary operations such as rack stripping
(6) Washing of equipment (e.g., pumps, filters, tanks)
(7) Cooling water used in heat exchangers to cool solutions in electroplating processes.

Rinsing

A large portion (perhaps 90 percent) of the water usage is in the rinsing operations. That used as cooling water is usually reused for rinsing. The water is used to rinse away the films of processing solutions from the surface of the work pieces. In performing this task, the water is contaminated by the operating solutions and is not directly reusable. Thus, the cost of water is an operating expense. Aqueous solutions result from the raw waste from each operation. Therefore, the location of rinse steps is important relative to the operations performed in the electroplating process. The general outline of operations in the processes was given in Tables 3 to 7.

Figures 2 and 3 schematically illustrate the flow for work pieces being processed and show the sites of water usage for rinsing. Figure 2 shows the minimum number of operations and the water flow in the wide practice of decorative chromium plating. However, there is no fixed relation between water usage and amount of work processed. Some plants use more water than the minimum required to maintain good quality work.

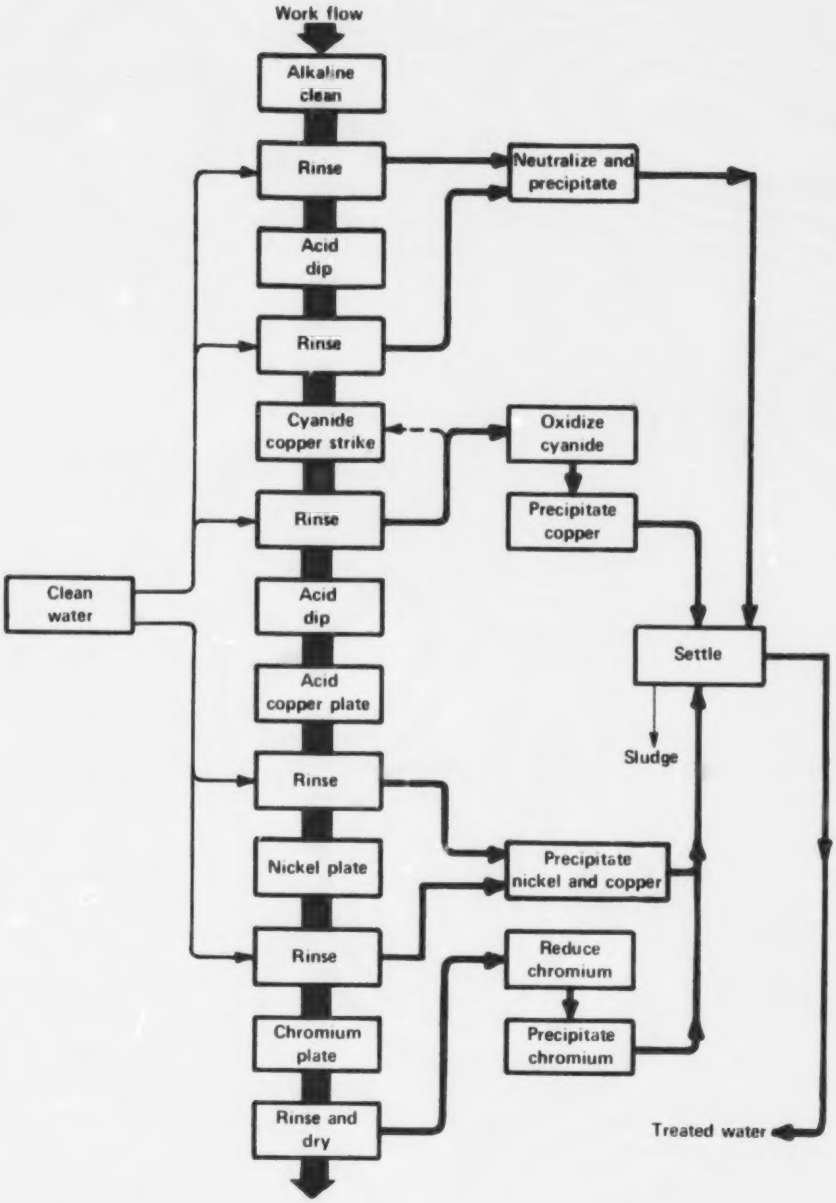
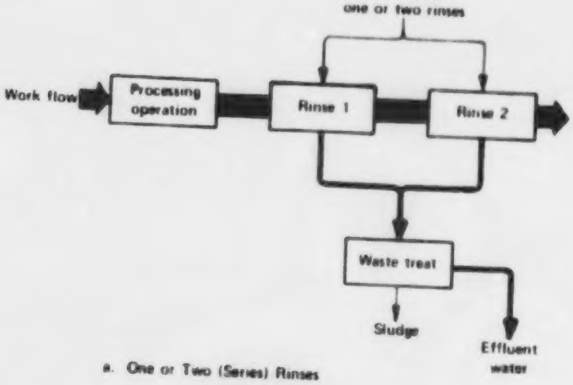
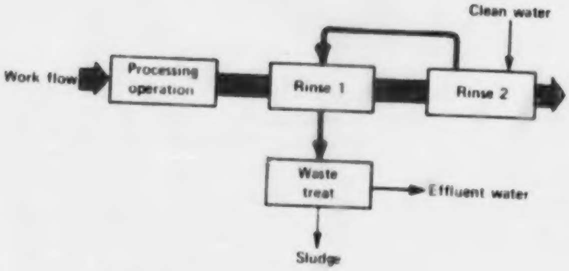

Work flow
Alkaline clean
Rinse
Neutralize and precipitate
Acid dip
Rinse
Cyanide copper strike
Oxidize cyanide
Rinse
Precipitate copper
Clean water
Acid dip
Settle
Acid copper plate
Sludge
Rinse
Nickel plate
Precipitate nickel and copper
Rinse
Reduce chromium
Chromium plate
Precipitate chromium
Rinse and dry
Treated water

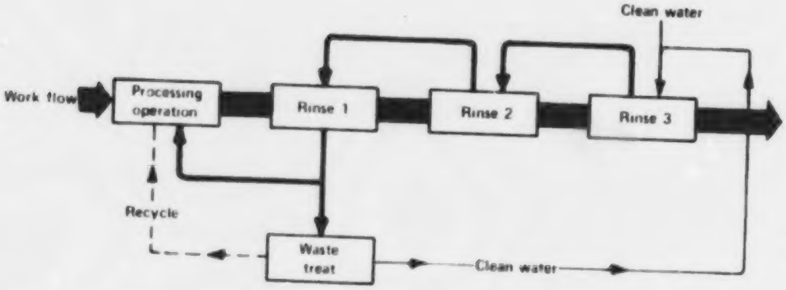
FIGURE 2. SCHEMATIC FLOW CHART FOR WATER FLOW IN CHROMIUM PLATING ZINC DIE CASTINGS, DECORATIVE


Clean water
one or two rinses
Work flow
Processing operation
Rinse 1
Rinse 2
Waste treat
Sludge
Effluent water

a. One or Two (Series) Rinses


Clean water
Work flow
Processing operation
Rinse 1
Rinse 2
Waste treat
Effluent water
Sludge

b. Two Counter Flow Rinses


Clean water
Work flow
Processing operation
Rinse 1
Rinse 2
Rinse 3
Recycle
Waste treat
Clean water

c. Three Counter Flow Rinses

FIGURE 3 ALTERNATIVE METHODS OF RINSING AFTER A PROCESSING OPERATION

Tables 3 to 7 show other processes which have an analogous water use for each operation of cleaning, acid dipping, plating, and rinsing according to one of the schemes in Figure 3.

Spills and Air Scrubbing

The water from washing away spills and washing down ventilation exhaust air is added to the chemically corresponding rinse water for treatment.

Dumps

Operating solutions to be dumped are slowly trickled into rinse water following the operation and prior to treatment. Alternatively, the operating solutions, which are much more concentrated than the rinse water, may be processed batch-wise in a treating facility. Subsequent discussion of waste treatment of rinse water covers all the water in the facility.

Water from Auxiliary Operations

Auxiliary operations such as rack stripping utilize solutions containing acids or cyanide for removing metal deposited on rack tips. These solutions accumulate large concentrations of metals and are decanted or dumped at regular intervals. They should be slowly trickled into the appropriate rinse water stream that contains similar chemicals for ultimate treatment.

Washing Equipment

Water used for washing filters, pumps, and tanks picks up residues of concentrated solutions or salts and should be routed to the appropriate rinse water stream for chemical treatment.

Cooling Water

As noted previously cooling water used in heat exchangers for cooling electroplating solutions is usually routed to rinse tanks for water conservation purposes. If this practice is not adopted, exit water from cooling units should be checked for constituents of the plating solution to guard against the discharge of pollutants in the event of a leak into the cooling unit.

Quantity of Wastes

At least 95 percent of the products being electroplated (or electroformed) to provide resistance to corrosion, wear, and other destructive forces are processed in medium sized or large plants (4,000 to 5,000 in number), each deploying at least 11 kg/day (25 pounds/day) of raw waste into rinse water. The potentially toxic waste in the form of heavy metal salts and cyanide salts from these sources is approximately 340,000 kg/day (750,000 pounds/day). This is equivalent to about 110,000 kg/day (250,000 pounds/day) of heavy metal and cyanide ions. Of the total salts, about two-thirds or 228,000 kg/day (505,000 pounds/day) is contributed by copper, nickel, chromium, and zinc plating operations, as shown in Table 13.

Supplementing the chemicals listed in Table 13, at least 225,000 kg/day (500,000 pounds/day) of alkalies and 450,000 kg/day (1,000,000 pounds/day) of acids are contributed to the total waste by cleaning and pickling operations that precede copper, nickel, chromium, and zinc plating. The proportion of phosphates in alkaline cleaning chemicals is unknown, but is believed to be 25 percent of the total alkalies.

Some of the alkaline solution waste and nearly all of the acid solution waste contain metals resulting from the dissolution of metal products to be plated. Hence, the total amount of wastewater constituents generated by copper, nickel, chromium, and zinc electroplating probably exceeds 900,000 kg/day (2,000,000 pounds/day).

From the estimated plating salts in Table 13, the total metal and cyanide load was estimated as follows:

Copper	11,000 kg/day	(24,000 pounds/day)
Nickel	12,000 kg/day	(27,000 pounds/day)
Chromium	25,000 kg/day	(55,000 pounds/day)
Zinc	19,000 kg/day	(42,000 pounds/day)
Cyanide	46,000 kg/day	(102,000 pounds/day)
TOTAL	113,000 kg/day	(250,000 pounds/day)

The estimated alkali load of 230,000 kg/day (500,000 pounds/day) and acid load of 450,000 kg day (1,000,000 pounds/ day) are usually in about the same ratio in most plants (i.e., combined acid/alkali wastewaters are mostly acid). Assuming the alkalinity as sodium hydroxide (NaOH) and acidity as sulfuric acid (H_2SO_4), combination/neutralization (about 0.9 kg NaOH/kg H_2SO_4) would indicate a total net acid load of 350,000 kg/day (750,000 pounds/day).

Sources of Waste

In electroplating facilities the wastes are derived from the material plated (discussed in Section IV) and the operating solutions. The principal ionic constituents of wastewater from plating on five basis materials are listed in Tables 14 to 18. Wastes associated with preparation for plating, electroplating, and postplating are combined in these tables. These operations are discussed below in more detail.

TABLE 13 ESTIMATED DAILY RAW WASTE LOAD OF PRINCIPAL SALTS USED IN COPPER, NICKEL, CHROMIUM, ZINC PLATING AND RELATED PROCESSES[a]

	Principal Salts			Percent of Total Salts Consumed by Plating
Operation	Identity	kg/day	pounds/day	
Copper plating	Copper cyanide, sodium cyanide, and copper sulfate	54,000	120,000	13
Nickel plating	Nickel chloride and nickel sulfate	54,000	120,000	17
Chromium plating	Chromic acid	45,000	100,000	13
Zinc plating	Zinc oxide, zinc cyanide, sodium cyanide, and zinc sulfate	68,000	150,000	23
Zinc chromating	Sodium chromate and sodium dichromate	6,800	15,000	2
		227,800	505,000	68

(a) Data from a survey conducted by Battelle's Columbus Laboratories in 1965.

TABLE 14. PRINCIPAL WASTEWATER CONSTITUENTS IN WASTES FROM PROCESSES FOR PLATING ON STEELS*

Constituent	1	2	3	4	5	6	7	8
Iron, ferrous, Fe^{+2}	X	X	X	X	X	X	X	X
Copper, cuprous, Cu^{+1}							X	
Copper, cupric, Cu^{+2}	X	X		X			X	
Nickel, Ni^{+2}	X	X		X				X
Chromium, chromate, Cr^{+6}	X	X	X			X		
Chromium, chromic, Cr^{+3}	X	X	X			X		
Zinc, Zn^{+2}					X	X		
Cyanide, CN^{-1}	X				X		X	
Sulfate, SO_4^{-2}	X	X	X	X	X	X	X	X
Chloride, Cl^{-1}	X	X	X	X	X	X	X	X
Carbonate, CO_3^{-2}		X	X	X	X	X	X	
Silicate, SiO_3^{-2}	X	X	X	X	X	X	X	X
Phosphate, PO_4^{-3}	X	X	X	X	X	X	X	X
Fluoborate, BF_6^{-1}								
Sulfamate, $NH_2SO_3^{-1}$	X	X		X				X
Nitrate, NO_3^{-1}								
Ammonium, NH_4^{+1}								
Organics	X	X		X			X	X

* Process numbers correspond to those in Table 2.

TABLE 15. PRINCIPAL WASTEWATER CONSTITUENTS IN WASTE FROM PROCESSES FOR PLATING ON ZINC DIE CASTINGS*

Constituent	1	2	3	4
Fe^{+2}				
Cu^{+1}				
Cu^{+2}	X			
Ni^{+2}	X			
Cr^{+6}	X		X	
Cr^{+3}	X		X	
Zn^{+2}	X	X		
CN^{-1}	X			
SO_4^{-2}	X	X	X	
Cl^{-1}				
$CO_3{}^{-2}$	X	X	X	
$SiO_3{}^{-2}$	X	X	X	
$PO_4{}^{-3}$	X	X	X	
$BF_6{}^{-1}$				
$NH_2SO_3{}^{-1}$				
$NO_3{}^{-1}$				
$NH_4{}^{+1}$				
Organics	X	X		

* Processes correspond to those in Table 3.

TABLE 16. PRINCIPAL WASTEWATER CONSTITUENTS IN WASTE FROM PROCESSES FOR PLATING ON BRASS*

Constituent	1	2	3	4
Fe^{+3}				
Cu^{+1}				
Cu^{+2}	X	X	X	X
Ni^{+2}	X	X	X	X
Cr^{+6}	X	X	X	
Cr^{+3}	X	X	X	
Zn^{+2}	X	X	X	
CN^{-1}	X	X	X	X
SO_4^{-2}				
Cl^{-1}	X		X	X
CO_3^{-2}	X	X	X	X
SiO_3^{-2}	X	X	X	X
PO_4^{-3}	X	X	X	X
BF_6^{-1}				
$NH_2SO_3^{-1}$				
NO_3^{-1}	X	X	X	X
NH_4^{+1}				
Organics	X	X	X	X

* Processes correspond to those in Table 4.

TABLE 17. PRINCIPAL WASTEWATER CONSTITUENTS IN WASTE FROM PROCESSES FOR PLATING ON ALUMINUM*

Constituent	1	2	3	4	5
Fe^{+3}					
Cu^{+1}					
Cu^{+2}					
Ni^{+2}	X				
Cr^{+6}	X	X	X		
Cr^{+3}	X	X	X		
Zn^{+2}	X	X			
Aluminum, Al^{+3}	X	X	X		
CN^{-1}					
SO_4^{-2}					
Cl^{-1}	X	X	X		
CO_3^{-2}	X	X	X		
SiO_3^{-2}	X	X	X		
PO_4^{-3}					
BF_6^{-1}	X	X	X		
$NH_2SO_3^{-1}$					
NO_3^{-1}					
NH_3^{-1}					
Organics	X				

* Processes correspond to those in Table 5.

TABLE 18. PRINCIPAL WASTEWATER CONSTITUENTS IN WASTE FROM PROCESSES FOR PLATING ON PLASTICS*

Constituent	1	2	3	4
Fe^{+3}				
Cu^{+1}				
Cu^{+2}	X	X	X	
Ni^{+2}	X	X	X	X
Cr^{+6}	X	X		
Cr^{+3}	X	X		
Zn^{+2}				
Tin, Sn^{+2}	X	X	X	X
Palladium, Pd^{+2}	X	X	X	X
CN^{-1}				
$SO_4{}^{-1}$	X	X	X	X
Cl^{-1}				
$CO_3{}^{-2}$	X	X	X	X
$SiO_3{}^{-2}$	X	X	X	X
$PO_4{}^{-3}$				
$BF_6{}^{-1}$				
Organics				
$NO_3{}^{-1}$				
$NH_3{}^{-1}$				

* Processes correspond to those in Table 6.

Preparation for Plating

Wastewater constituents derived from the chemicals generally utilized for preplate preparation solutions or from reactions with the common basis materials processed in these solutions are as follows:

- Alkyl aryl oxyalcohols
- Alkyl aryl sulfonates
- Aluminum chloride
- Aluminum nitrate
- Aluminum sulfate
- Chromic acid
- Copper chloride
- Copper fluoborate
- Copper nitrate
- Copper sulfate
- Ferric chloride
- Ferric phosphate
- Ferric sulfate
- Ferrous chloride
- Ferrous phosphate
- Ferrous sulfate
- Fluoboric acid
- Hydrochloric acid
- Nitric acid
- Phosphoric acid
- Sodium bisulfate
- Sodium borate
- Sodium carbonate
- Sodium hexametaphosphate
- Sodium hydroxide
- Sodium metosilicate
- Sodium orthosilicate
- Sodium pyrophosphate
- Sodium sulfate
- Sodium triphosphate
- Stannous chloride
- Sulfamic acid
- Sulfuric acid
- Zinc chloride
- Zinc sulfate

Solutions of all of the above chemicals containing acids and alkalies must be neutralized prior to discharge into navigable waters. All of the metals may be removed to varying degrees by the treatment techniques discussed in Section VII.

Alkaline Cleaners. Regardless of the material to be electroplated, cleaners are made up with one or more of the following chemicals: sodium hydroxide, sodium carbonate, sodium metasilicate, sodium phosphate (di- or trisodium), sodium silicate, sodium tetraphosphate, and a wetting agent. Compositions for steel are more alkaline and active than those for brass, zinc die castings, and aluminum. Soils to be removed from basis materials by cleaners are unrelated chemically to the metal and usually are the same general type. The need for variation in cleaner composition is partly based on the nature of the soil and on the chemical resistance of the material being prepared for plating.

In addition to the chemicals comprising the alkaline cleaners, rinses and spills, wastes contain soaps from emulsification of certain greases left on basis material surfaces from polishing and buffing that precede electroplating. Also, emulsified oils are likely to be present. The raw wastes from the basis materials and process solutions prior to plating show up in the rinse waters, spills, dumps of concentrated processing solution, wash waters from air-exhaust ducts, and leaky heating and cooling coils and heat exchangers.

Acid Dips. Acid dips are chosen to accommodate the basis material. Acid solutions are made up with one or more of the following: hydrochloric acid, sulfuric acid, phosphoric acid, fluoboric acid, chromic acid, and nitric acid. The solution compositions vary according to nature of any tarnish or scale, chemically related to the metal and to the resistance of the material to chemical reaction with the acid solution. The acid-treating baths for preparing metal substrates for plating usually have a relatively short finite life. When used solutions are replaced with fresh solutions, large amounts of chemicals must be treated or reclaimed. Water used for rinsing after acid treating also collects heavy metal waste by dragout of solution from the acid-treating tank.

Acid solutions used for pickling, acid dipping, or activating accumulate appreciable amounts of metals, as a result of metal dissolution from metallic work pieces and/or uncoated areas of plating racks that are recycled repeatedly through the cleaning, acid treating, and electroplating cycle. In barrel zinc-plating operations, the amount of zinc dissolved in the acid-treating solution from the danglers used to make electrical contact to the work pieces sometimes equals the amount of zinc carried over into the water rinse solution following the zinc-plating bath. The copper (and zinc) accumulated in acid bright dip solutions used to prepare electrical copper and brass contacts for plating can exceed in amount the metal contributed to rinse-water waste by dragout from the plating bath.

The amount of waste contributed by preplate preparation steps varies appreciably from one facility to another, depending on the substrate material, the formulation of the solution adopted for cleaning or activating the material, the solution temperature, the cycle time, and other factors. The initial condition of the substrate material affects the amount of waste generated during preplate treatment. A dense, scalefree copper alloy article can be easily prepared for plating by using a mild hydrochloric acid solution that dissolves little or no copper, whereas products with a heavy scale require stronger and hotter solutions and longer treating periods to insure the complete removal of any oxide, prior to plating.

Electroplating

Wastewater constituents derived from solutions generally used for electroplating copper, nickel, chromium, and zinc are as follows:

Alkylaryl sulfonates
Aluminum chloride
Aluminum sulfate
Ammonium chloride
Boric acid

Potassium hydroxide
Rochelle Salts
Saccharin
Sodium bicarbonate
Sodium carbonate

Chromic acid
Coumarin
Copper cyanide
Copper sulfate
Fluoboric acid
Fluosilicic acid
Hydrochloric acid
Nickel chloride
Nickel fluoborate
Nickel sulfamate
Nickel sulfate
Potassium cyanide
Sodium cyanide
Sodium ethylene diamine tetraacetic acid
Sodium fluosilicate
Sodium hydroxide
Sodium pyrophosphate
Zinc chloride
Zinc cyanide
Zinc fluoborate
Zinc oxide
Zinc sulfate
Sulfuric acid

Prior to end-of-process discharge, solutions containing alkalies and acids (or acid salts) must be neutralized. All of the metals must be removed to the specified levels by the technology detailed in Section VII.

Copper Plating. Copper is electroplated from four types of baths, i.e., alkaline cyanide, acid sulfate, pyrophosphate, and fluoborate, which are prepared with a corresponding copper salt. The cyanide solutions also contain sodium carbonate and may also contain sodium hydroxide or sodium potassium tartrate. All four types may also contain a small amount of an organic chemical for refining the grain or brightening the plate. Typical compositions are cited in References (2) and (3). Cyanide solutions are used extensively for copper plating, but acid copper solutions have been adopted for plating large numbers of steel, plastic, and zinc alloy products. Steel and zinc are customarily plated first in a cyanide strike bath to insure good electroplate adhesion. Copper plating solutions are rarely dumped, so the principal source of waste is the rinse water used to remove the solution that remains on work surfaces (dragout) after copper-plated articles are removed from the plating tank. Rinsing between cyanide copper striking and plating in a concentrated cyanide bath is not required, so facilities equipped with both kinds of solutions create just one source of waste, in comparison with others equipped with a cyanide strike and an acid bath. Even so, some companies prefer the cyanide strike-acid copper sequence for minimizing the amount of cyanide waste requiring treatment by chemical oxidation or for improving the quality of their products.

A secondary source of waste in a typical copper plating facility is associated with solution filtration. Filters, pumps, and pipes commonly develop leaks, classified as spills. Not all of the solution is washed back into the plating tank when filter cartridges or bags are exchanged for new ones (or washed free of contaminating solids that reduce the filtration rate). The high-concentration cyanide and acid copper sulfate solutions are usually filtered continuously, in order to prevent rough deposits.

A nickel strike for steel has been adopted by some companies choosing to eliminate cyanide baths. The acid copper sulfate bath can then be used over the nickel strike, in a sequence similar to that adopted for copper plating on plastic which is first metallized by a thin film of electroless nickel. A satisfactory nickel strike has not been identified for zinc die castings, which are universally plated first with a cyanide copper strike. Copper is extensively electroplated in combination with nickel and chromium. About 75 percent of the copper anode consumption (18,000,000 kg/year or 40,000,000 pounds/year) is expended for this purpose, but other applications account for significant quantities. For example, printed circuit boards are copper plated to make through-hole electrical contacts between circuits on opposite sides of the boards. Another significant activity is copper electroforming (including electrotyping). Some facilities installed for electroplating cabinet hardware (principally steel and zinc alloy die castings) utilize copper plating as the only deposition step, to produce colored finishes.

Nickel Plating. Nickel is electroplated from Watts (sulfate-chloride-boric acid), sulfamate, chloride, and fluoborate baths. Each type of solution is prepared with the corresponding nickel salt, a buffer such as boric acid and a small concentration of a wetting agent. A small amount of another organic chemical may be added to brighten the deposits or control another property. Nickel is extensively electroplated in a three-metal composite coating of copper, nickel, and chromium. In the best practice, nickel plating would follow copper plating without drying as in Processes 1 and 2, Table 4. Nickel also is electrodeposited on steel for decorative-protective finishes and on other materials for electroforming. In these applications, nickel plating is preceded by cleaning and activating operations in a sequence selected for a specific basis material. Nickel electroplate is freshly plated and rinsed without drying and directly chromium plated according to processes shown in Tables 3 through 7. Typical solution compositions are given in References 2 and 3.

In addition to the constituents of new solutions, used solutions contain small concentrations of other heavy metals, depending on the kind of material being processed. For example, the nickel bath gradually picks up copper and zinc when copper-plated steel and copper-plated zinc die castings are being nickel plated. Only periodic analyses will reveal the amounts present.

Organic agents that refine the grain size of the deposit and brighten the plate are added to all nickel plating baths adopted for sequential nickel-chromium plating. Proprietary agents are supplied by metal finishing supply companies that have developed stable, effective chemicals for insuring mirror-like, corrosion-protective deposits requiring no buffing. Aryl polysulfonates, sulfonamides, and sulfinimides such as napthylene disulfonic acid, p-toluene sulfonamide, and saccharin are examples of one class of brightening agents frequently combined with a sulfonated aryl aldehyde, ethylene sulfonamide, amine, nitrile, imide, azo dye, or another special compound. These organic chemicals and the surface active agents (typically sodium lauryl sulfate) customarily added to reduce surface tension and prevent pitting contribute small concentrations that impose a small COD to the water rinse step following nickel plating. Because the organic compounds are customarily added to nickel plating baths in small concentrations (0.5 to 3 g/l), their total concentration in the untreated rinse water seldom exceeds 4 mg/l.

Leakage from filters, pumps, and pipes is a secondary source of nickel waste, although some filters are equipped to recover and recycle leaks that occur from the pump and filter. Incomplete washing of filter cartridges, bags, or plates during filter maintenance is another source of waste. Continuous filtration of the nickel solution is adopted for preventing roughness by most of the companies engaged in nickel plating. Filters sometimes are packed with activated carbon for removing organic impurities that degrade the characteristics or properties of the deposit.

The relatively high value of nickel has encouraged the adoption of in-process controls for minimizing dragout into the rinse water following nickel plating, which is the major source of waste. Nickel plating baths are rarely dumped.

Chromium Plating. All chromium plating solutions contain chromic acid and a small amount of sulfuric acid or a mixture of sulfuric acid and fluosilicate or fluoride ions. The concentration of chromic acid usually is two orders of magnitude higher than the concentration of the other materials. Three basis materials account for the bulk of the work: steel, nickel-electroplated steel, and nickel-electroplated zinc. Solutions containing 150 to 400 g/l of chromic acid are the common baths for electroplating 0.2 to 1.0m (0.000008 to 0.00040 inch) of decorative chromium or hard chromium on steel and aluminum for resisting wear. Unlike the copper and nickel plating processes which utilize soluble copper or nickel anodes to replenish in solution the metal deposited on the work pieces, chromium plating processes always use insoluble lead alloy anodes. Thus, some portion of the chromic acid added regularly for maintenance is consumed by reduction to chromium metal at cathode surfaces. This proportion varies from only 10 to 20 percent in decorative chromium plating facilities to the range of 25 to 90 percent in hard chromium installations, depending on the in-process controls adopted for reducing the dragout loss to the rinse water.

Dragout into rinse water is the major source of raw waste. Spray carried from the solution by the hydrogen gas generated at cathode surfaces and oxygen gas produced at anode surfaces is a significant secondary source. Chromium plating process tanks are customarily vented to protect workers from this spray, so an appreciable amount of chromic acid is carried into air ducts in the form of aerosols released to the atmosphere. Air scrubbers are incorporated in the exhaust systems installed in some plants to recover this source of waste and recycle it to the chromium plating bath.

Zinc Plating. Zinc is electroplated in cyanide solutions containing sodium cyanide, zinc oxide or cyanide and sodium hydroxide; noncyanide alkaline solutions prepared with zinc pyrophosphate or another chelating agent such as tetrasodium pyrophosphate, sodium citrate or the sodium salt of ethylene diamine tetraacetic acid; acid or neutral chloride baths prepared with zinc chloride and a buffer salt such as ammonium chloride; or acid sulfate solutions containing zinc sulfate and a buffer salt such as aluminum chloride or sulfate. A small concentration of an organic compound such as glucose, licorice, or glycerin may be added to the chloride or sulfate baths for brightening purposes. Formulations for these solutions are given in References (2) and (3).

In addition to dragout of solution into rinse water which is the major source of waste, zinc waste is generated during continuous or batch filtration. Air agitation and hydrogen gas evolution at cathode surfaces create aerosol particles carried through exhaust systems into the atmosphere, unless removed by wash water that is combined with the rinse water for treatment.

Postplating Treatments

Postplating treatment is rare for nickel and chromium- plated products, but a large portion of zinc-plated steel and a smaller portion of copper-plated products are processed to impart a chromate film or one of several alternative colored finishes. Chemicals utilized for preparing postplating treatment solutions for copper and zinc electroplates or derived by reactions with the electroplated metal include the following:

- Ammonium carbonate
- Ammonium hydroxide
- Ammonium molybdate
- Ammonium persulfate
- Barium sulfide
- Chromic acid
- Copper acetate
- Copper chloride
- Copper nitrate
- Copper sulfate
- Ferric chloride
- Ferrous sulfate
- Hydrochloric acid
- Nickel chloride
- Nickel sulfate
- Nitric acid
- Phosphoric acid
- Potassium chlorate
- Potassium nitrate
- Potassium permanganate
- Sodium dichromate
- Sodium hydroxide
- Sodium polysulfide
- Sodium sulfide
- Sodium thiocyanate
- Sulfuric acid
- Zinc nitrate

A dilute solution of nitric acid is an example of a bright dip bath for zinc plate. A chromate solution for zinc is always acidic and contains hexavalent chromium compounds, such as chromic acid, and contains inorganic and organic compounds as activators or catalysts known only to the suppliers. Both types of posttreatment solutions accumulate dissolved zinc and require dumping and replacement at regular intervals, thereby creating waste that must be treated prior to discharge. Used chromate-filming solutions also contribute trivalent and hexavalent chromium ions to wastewater. Water rinsing operations after bright dipping or chromating also are sources for waste.

Copper (and brass) plated steel and zinc alloy, and zinc-plated products are sometimes oxidized or otherwise treated in solutions that produce attractive, desired colors such as those described in Reference (3). Some of these solutions are prepared with copper or other heavy metal salts. Others accumulate dissolved copper or zinc as a result of use, some of which show up in rinse water associated with the post treatment. Furthermore, all have a finite bath life and must be replaced at intervals, like the bright-dip and chromate-filming solutions used for treating zinc.

Decorative colors are applied on copper and zinc, after electroplating. Operators frequently develop their own solution compositions. The following formulation indicate the general nature of such solutions.

Brown on copper:

Potassium chlorate, $KClO_3$ - 40 g/l (5.5 oz/gal)

Nickel sulfate, $Ni_2SO_4 \cdot 6H_2O$ - 20 g/l (2.75 oz/gal)

Copper sulfate, $CuSO_4 \cdot 6H_2O$ - 190 g/l (24.0 oz/gal)

Light brown on copper:

Barium sulfide, BaS_3 - 4 g/l (0.5 oz/gal)

Ammonium carbonate, $(NH_4)2CO_3$ - 2 g/l (0.25 oz/gal)

Verde green on copper:

Copper nitrate, $Cu(NO_3)_2$ - 30 g/l (4 oz/gal)

Ammonium chloride, NH_4Cl_3 - 30 g/l (4 oz/gal)

Calcium chloride, $CaCl_2$ - 30 g/l (4 oz/gal)

Black on zinc:

Ammonium molybdate, NH_4MoO_4 - 30 g/l (4 oz/gal)

Ammonia, NH_3 - 47 mg/l (6 fluid oz/gal)

or Copper sulfate, $CuSO_4 \cdot 6H_2O$ - 45 g/l (6 oz/gal)

Potassium chloride, KCl - 45 g/l (6 oz/gal)

Brown on zinc:

Double nickel salts, $(NH_4)2SO_4 \cdot NiSO_4$ - 4 g/l (0.5 oz/gal)

Copper sulfate, $CuSO_4 \cdot 6H_2O$ - 4 g/l (0.5 oz/gal)

Potassium chlorate, $KClO_3$ - 4 g/l (0.5 oz/gal)

SECTION VI

SELECTION OF POLLUTANT PARAMETERS

Introduction

This section of the report reviews the waste characterization detailed in Section V and identifies in terms of chemical, physical, and biological constituents that which constitutes pollutants as defined in the act. Rationale for the selection of wastewater constituents as pollutants is presented.

First, consideration was given to the broad range of chemicals used in the metal finishing industry. Constituents associated with the subcategory of electroplating and limited to copper, nickel, chromium and zinc plating were considered in detail. Those considered to be potentially toxic pollutants are identified. Other constituents were examined in the light of their probable concentration in untreated wastewater in relation to water quality criteria for discharge, in order to form a judgment on pollutants to be monitored.

Specific consideration is given in this section to defining the physical form of metals to be considered pollutants, as well as definition of analytical techniques for reporting their concentrations in the wastewater discharge.

Metal Finishing Wastewater Constituents

A large variety of chemicals used in the metal finishing industry become wastewater constituents. The important wastewater constituents for electroplating copper, nickel, chromium, and zinc were identified in Section V. Not all of these constituents will be found in the wastewaters from every facility since the number of metals plated in a single facility varies as well as the number of basic metals pretreated and types of posttreatment operations. Metal finishing operations other than electroplating and other electroplating operations than copper, nickel, chromium, and zinc would contribute other metal ions. When present, these other metal ions are usually coprecipitated with copper, nickel, chromium, and/or zinc unless they are heavy metal pollutants of greater potential toxicity requiring special control and treatment technology. The nonmetallic cations and anions from electroplating copper, nickel, chromium, and zinc can be considered typical of the metal finishing industry.

Electroplating Wastewater Constituents

The wastewater constituents from electroplating copper, nickel, chromium, and zinc were identified qualitatively in Section V.

Preceding page blank

Each wastewater constituent is additive to the concentration of that constituent in the raw water supply if the latter is not deionized. Sometimes constituents in the effluent originate from the raw water supply.

Table 19 shows approximate quantitative values for a typical facility plating copper, nickel, chromium, and zinc (Plant 33-1) with no other metal plating or metal finishing operations other than electroplating. The values represent the combined raw waste effluent assuming no treatment and include both chemicals in wastewater from rinses and concentrated solution dumps collected and metered uniformly into the wastewater. Good chemical treatment will oxidize over 99 percent of the cyanide and normally remove 85 to 99 percent of the metals. The other constituents in the raw waste having much higher solubilities than metal hydroxides are usually not removed, and contribute to the total dissolved solids of the treated effluent.

Some soluble constituents are adsorbed on the insoluble material and removed during clarification. The concentrations of total dissolved solids and each soluble constituent depend on the degree of water conservation used in the facility. The concentrations shown in Table 19 are considered representative of the average electroplating facility.

TABLE 19. APPROXIMATE CONCENTRATIONS OF WASTEWATER CONSTITUENTS PRIOR TO TREATMENT FROM A TYPICAL FACILITY ELECTROPLATING COPPER, NICKEL, CHROMIUM, AND ZINC (PLANT 33-1)

Wastewater Constituent	Estimated Untreated Wastewater Concentration, mg/l	Analysis of Treated Effluent Concentration, mg/l	Water Supply Analysis, mg/l
Copper (Cu^+ or Cu^{2+})	6.7	0.23	
Nickel (Ni^{+2})	2.4	<0.20	
Chromium (Cr^{3+})	0.05	0.15	
(Cr^{6+})	17	<0.05	
(Cr_T)	17	<0.20	
Zinc (Zn^{2+})	32	0.1	
Cyanide (CN^-)	50	0.21	
Sodium (Na^+)	465		20
Potassium (K^+)	2.4		
Carbonate ($CO_3{}^{2-}$)	57		
Orthophosphate ($PO_4{}^{3-}$)	47	3.0	<0.01
Pyrophosphate ($P_2O_7{}^{4-}$)	53		
Silicate ($SiO_3{}^{2-}$)	50		
Metaborate ($BO_2{}^{3-}$)	36		
Perborate ($BO_3{}^{3-}$)	1.3		
Sulfate ($SO_4{}^{2-}$)	19		20
Bisulfate (HSO_4)	3.7		
Fluoride (F^-)	0.1		0.1
Fluosilicate ($SiF_6{}^{2-}$)	0.5		
Tartrate ($C_4H_4O_6{}^{2-}$)	8.9		
Chloride (Cl^-)	228		25
Nitrate ($NO_3{}^-$)	1.4		
Wetting agents (organic)	6.8		
Sequestrants	6.5		
Chelates	6.5		
Additives (organic)	0.5		
Proprietary acid salts	32		
Total dissolved solids	1150.		

Wastewater Constituents and Parameters of Pollutional Significance

The wastewater constituents of pollutional significance for this segment of the electroplating industry include copper, nickel, chromium, zinc, cyanide, suspended solids, and pH. It is recommended that copper, nickel, chromium, zinc, and cyanide be the subject of effluent limitations and standards of performance for the electroplating industry regardless of the physical form (soluble or insoluble metal) or chemical form (e.g., valence state of metal or type of cyanide complex). All other metals and chemical compounds in the wastewater that are not yet specifically the subject of effluent limitations but which would normally be precipitated during treatment for removal of copper, nickel, chromium, and zinc are considered part of the suspended solids as well as any chemical or biological material adsorbed or entrapped by the suspended solids during clarification and separation. Thus, suspended solids are a wastewater constituent of pollutional significance.

The pH is subject to effluent limitations because it affects the solubility of metallic compounds such as zinc hydroxide and the soluble metal content of the treated effluent.

Thus, the major chemical, physical, and biological wastewater constituents and parameters of pollutional significance are as follows:

Copper
Nickel
Chromium, hexavalent
Chromium, total
Zinc
Cyanide, amenable to oxidation by chlorine
Cyanide, total
Suspended solids
pH

Other wastewater constituents of secondary importance in the electroplating industry that are not the subject of effluent limitations or standards of performance are as follows:

Total dissolved solids
Chemical oxygen demand
Biochemical oxygen demand
Oil and grease
Turbidity
Color
Temperature

Rationale for the Selection of Wastewater Constituents and Parameters

Copper

Copper salts occur in natural surface waters only in trace amounts, up to about 0.05 mg/l, so that their presence generally is the result of pollution.

Copper is not considered to be a cumulative systemic poison for humans, but it can cause symptoms of gastroenteritis, with nausea and intestinal irritations, at relatively low dosages. The limiting factor in domestic water supplies is taste. Threshold concentrations for taste have been generally reported in the range of 1.0-2.0 mg/l of copper, while as much as 5-7.5 mg/l makes the water completely unpalatable.

The toxicity of copper to aquatic organisms varies significantly, not only with the species, but also with the physical and chemical characteristics of the water, including temperature, hardness, turbidity, and carbon dioxide content. In hard water, the toxicity of copper salts is reduced by the precipitation of copper carbonate or other insoluble compounds. The sulfates of copper and zinc, and of copper and cadmium are synergistic in their toxic effect on fish.

Copper concentrations less than 1 mg/l have been reported to be toxic, particularly in soft water, to many kinds of fish, crustaceans, mollusks, insects, phytoplankton and zooplankton. Concentrations of copper, for example, are detrimental to some oysters above .1 mg/l. Oysters cultured in sea water containing 0.13-0.5 mg/l of copper deposited the metal in their bodies and became unfit as a food substance.

Nickel

Elemental nickel seldom occurs in nature, but nickel compounds are found in many ores and minerals. As a pure metal it is not a problem in water pollution because it is not affected by, or soluble in, water. Many nickel salts, however, are highly soluble in water.

Nickel is extremely toxic to citrus plants. It is found in many soils in California, generally in insoluble form, but excessive acidification of such soil may render it soluble, causing severe injury to or the death of plants. Many experiments with plants in solution cultures have shown that nickel at 0.5 to 1.0 mg/l is inhibitory to growth.

Nickel salts can kill fish at very low concentrations. Data for the fathead minnow show death occurring in the range of 5-43 mg/l, depending on the alkalinity of the water.

Nickel is present in coastal and open ocean concentrations in the range of 0.1 - 6.0 ug/l, although the most common values are 2 - 3 ug/l. Marine animals contain up to 400 ug/l, and marine plants contain up to 3,000 ug/l. The lethal limit of nickel to some marine fish has been reported as low as 0.8 mg/l. Concentrations of 13.1 mg/l have been reported to cause a 50 percent reduction of the photosynthetic activity in the giant kelp (*Macrocystis pyrifera*) in 96 hours, and a low concentration was found to kill oyster eggs.

Chromium

Chromium, in its various valence states, is hazardous to man. It can produce lung tumors when inhaled and induces skin sensitizations. Large doses of chromates have corrosive effects on the intestinal tract and can cause inflammation of the kidneys. Levels of chromate ions that have no effect on man appear to be so low as to prohibit determination to date.

The toxicity of chromium salts toward aquatic life varies widely with the species, temperature, pH, valence of the chromium, and synergistic or antagonistic effects, especially that of hardness. Fish are relatively tolerant of chromium salts, but fish food organisms and other lower forms of aquatic life are extremely sensitive. Chromium also inhibits the growth of algae.

In some agricultural crops, chromium can cause reduced growth or death of the crop. Adverse effects of low concentrations of chromium on corn, tobacco and sugar beets have been documented.

Hexavalent chromium is considered to be most active of the chromium species. Hexavalent chrome also is an indicator of the effectiveness of a chemical step to control total chromium.

Zinc

Occurring abundantly in rocks and ores, zinc is readily refined into a stable pure metal and is used extensively for galvanizing, in alloys, for electrical purposes, in printing plates, for dye-manufacture and for dyeing processes, and for many other industrial purposes. Zinc salts are used in paint pigments, cosmetics, pharmaceuticals, dyes, insecticides, and other products too numerous to list herein. Many of these salts (e.g., zinc chloride and zinc sulfate) are highly soluble in water; hence it is to be expected that zinc might occur in many industrial wastes. On the other hand, some zinc salts (zinc carbonate, zinc oxide, zinc sulfide) are insoluble in water and consequently it is to be expected that some zinc will precipitate and be removed readily in most natural waters.

In zinc-mining areas, zinc has been found in waters in concentrations as high as 50 mg/l and in effluents from metal-plating works and small-arms ammunition plants it may occur in significant concentrations. In most surface and ground waters, it is present only in trace amounts. There is some evidence that zinc ions are adsorbed strongly and permanently on silt, resulting in inactivation of the zinc.

Concentrations of zinc in excess of 5 mg/l in raw water used for drinking water supplies cause an undesirable taste which persists through conventional treatment. Zinc can have an adverse effect on man and animals at high concentrations.

In soft water, concentrations of zinc ranging from 0.1 to 1.0 mg/l have been reported to be lethal to fish. Zinc is thought to exert its toxic action by forming insoluble compounds with the mucous that covers the gills, by damage to the gill epithelium, or possibly by acting as an internal poison. The sensitivity of fish to zinc varies with species, age and condition, as well as with the physical and chemical characteristics of the water. Some acclimatization to the presence of zinc is possible. It has also been observed that the effects of zinc poisoning may not become apparent immediately, so that fish removed from zinc-contaminated to zinc-free water (after 4-6 hours of exposure to zinc) may die 48 hours later. The presence of copper in water may increase the toxicity of zinc to aquatic organisms, but the presence of calcium or hardness may decrease the relative toxicity.

Observed values for the distribution of zinc in ocean waters vary widely. The major concern with zinc compounds in marine waters is not one of acute toxicity, but rather of the long-term sub-lethal effects of the metallic compounds and complexes. From an acute toxicity point of view, invertebrate marine animals seem to be the most sensitive organisms tested. The growth of the sea urchin, for example, has been retarded by as little as 30 ug/l of zinc.

Zinc sulfate has also been found to be lethal to many plants, and it could impair agricultural uses.

Cyanide

Cyanides in water derive their toxicity primarily from undissolved hydrogen cyanide (HCN) rather than from the cyanide ion (CN^-). HCN dissociates in water into H^+ and CN^- in a pH-dependent reaction. At a pH of 7 or below, less than 1 percent of the cyanide is present as CN^-; at a pH of 8, 6.7 percent; at a pH of 9, 42 percent; and at a pH of 10, 87 percent of the cyanide is dissociated. The toxicity of cyanides is also increased by increases in temperature and reductions in oxygen tensions. A temperature rise of 10°C produced a two- to threefold increase in the rate of the lethal action of cyanide.

Cyanide has been shown to be poisonous to humans, and amounts over 18 mg/l can have adverse effects. A single dose of 50-60 mg is reported to be fatal.

Trout and other aquatic organisms are extremely sensitive to cyanide. Amounts as small as .1 mg/l can kill them. Certain metals, such as nickel, may complex with cyanide to reduce lethality especially at higher pH values, but zinc and cadmium cyanide complexes are exceedingly toxic.

When fish are poisoned by cyanide, the gills become considerably brighter in color than those of normal fish, owing to the inhibition by cyanide of the oxidase responsible for oxygen transfer from the blood to the tissues.

Total Suspended Solids

Suspended solids include both organic and inorganic materials. The inorganic components include sand, silt, and clay. The organic fraction includes such materials as grease, oil, tar, animal and vegetable fats, various fibers, sawdust, hair, and various materials from sewers. These solids may settle out rapidly and bottom deposits are often a mixture of both organic and inorganic solids. They adversely affect fisheries by covering the bottom of the stream or lake with a blanket of material that destroys the fish-food bottom fauna or the spawning ground of fish. Deposits containing organic materials may deplete bottom oxygen supplies and produce hydrogen sulfide, carbon dioxide, methane, and other noxious gases.

In raw water sources for domestic use, state and regional agencies generally specify that suspended solids in streams shall not be present in sufficient concentration to be objectionable or to interfere with normal treatment processes. Suspended solids in water may interfere with many industrial processes, and cause foaming in boilers, or encrustations on equipment exposed to water, especially as the temperature rises. Suspended solids are undesirable in water for textile industries; paper and pulp; beverages; dairy products; laundries; dyeing; photography; cooling systems, and power plants. Suspended particles also serve as a transport mechanism for pesticides and other substances which are readily adsorbed onto clay particles.

Solids may be suspended in water for a time, and then settle to the bed of the stream or lake. These settleable solids discharged with man's wastes may be inert, slowly biodegradable materials, or rapidly decomposable substances. While in suspension, they increase the turbidity of the water, reduce light penetration and impair the photosynthetic activity of aquatic plants.

Solids in suspension are aesthetically displeasing. When they settle to form sludge deposits on the stream or lake bed, they are often much more damaging to the life in water, and they retain the capacity to displease the senses. Solids, when transformed to sludge deposits, may do a variety of damaging things, including blanketing the stream or lake bed and thereby destroying the living spaces for those benthic organisms that would otherwise occupy the habitat. When of an organic and therefore decomposable nature, solids use a portion or all of the dissolved oxygen available in the area. Organic materials also serve as a seemingly inexhaustible food source for sludgeworms and associated organisms.

Turbidity is principally a measure of the light absorbing properties of suspended solids. It is frequently used as a substitute method of quickly estimating the total suspended solids when the concentration is relatively low.

pH, Acidity and Alkalinity

Acidity and alkalinity are reciprocal terms. Acidity is produced by substances that yield hydrogen ions upon hydrolysis and alkalinity is produced by substances that yield hydroxyl ions. The terms "total acidity" and "total alkalinity" are often used to express the buffering capacity of a solution. Acidity in natural waters is caused by carbon dioxide, mineral acids, weakly dissociated acids, and the salts of strong acids and weak bases. Alkalinity is caused by strong bases and the salts of strong alkalies and weak acids.

The term pH is a logarithmic expression of the concentration of hydrogen ions. At a pH of 7, the hydrogen and hydroxyl ion concentrations are essentially equal and the water is neutral. Lower pH values indicate acidity while higher values indicate alkalinity. The relationship between pH and acidity or alkalinity is not necessarily linear or direct.

Waters with a pH below 6.0 are corrosive to water works structures, distribution lines, and household plumbing fixtures and can thus add such constituents to drinking water as iron, copper, zinc, cadmium and lead. The hydrogen ion concentration can affect the "taste" of the water. At a low pH water tastes "sour". The bactericidal effect of chlorine is weakened as the pH increases, and it is advantageous to keep the pH close to 7. This is very significant for providing safe drinking water.

Extremes of pH or rapid pH changes can exert stress conditions or kill aquatic life outright. Dead fish, associated algal blooms, and foul stenches are aesthetic liabilities of any waterway. Even moderate changes from "acceptable" criteria limits of pH are deleterious to some species. The relative toxicity to aquatic life of many materials is increased by changes in the water pH. Metalocyanide complexes can increase a thousand-fold in toxicity with a drop of 1.5 pH units. The availability of many nutrient substances varies with the alkalinity and acidity. Ammonia is more lethal with a higher pH.

The lacrimal fluid of the human eye has a pH of approximately 7.0 and a deviation of 0.1 pH unit from the norm may result in eye irritation for the swimmer. Appreciable irritation will cause severe pain.

Rationale for Rejection of Other Wastewater Constituents as Pollutants

Metals

The rationale for rejection of any metal other than copper, nickel, chromium, and zinc as a pollutant is based on one or more of the following reasons:

(1) They would not be expected to be present in electroplating wastes from copper, nickel, chromium, and zinc plating processed in significant amounts (e.g., uranium, mercury, arsenic), or

(2) They will be removed simultaneously by coprecipitation and clarification along with copper, nickel, chromium, and/or zinc (e.g., iron), or

(3) They will be the subject of effluent limitations developed for other segments of the electroplating point source category. (e.g., electroplating of cadmium, tin, lead, silver, gold, platinum, palladium, iron, cobalt, and other metals and alloys) or

(4) Insufficient data exists upon which to base effluent limitations and standards of performance.

Dissolved Solids

Dissolved solids do not constitute an important parameter indicative of pollution when associated heavy metals are also the subject of effluent limitations. Although the concentration of total dissolved solids will become higher as efforts are directed to reducing water use and volume of effluent discharged, the total quantity of dissolved solids will remain unchanged.

Chemical Oxygen Demand

Chemical oxygen demand is not an important parameter in the electroplating industry because cyanide is controlled independently and the quantity of organic compounds or oxidizable inorganic compounds in the wastewater is very low.

Biochemical Oxygen Demand

Biochemical oxygen demand is usually not an important pollution parameter in the electroplating industry. An electroplating plant in a suburban location not discharging to a publicly owned system must treat its own sanitary sewage in a separate treatment facility. If the plant chooses to mix the treated sanitary effluent with electroplating wastes prior to treatment, BOD would be considered a major parameter.

Oil and Grease

Oil and grease is not normally a significant pollution parameter in the electroplating industry because these materials are removed from workpieces by nonaqueous solvents. Added pollution reduction is usually achieved by the usual practice of installing oil and grease skimmers on settling tanks. Where such control practices are absent, oil and grease might be considered a parameter subject to control and measurement.

Turbidity

Turbidity is indirectly measured and controlled independently by the limitation on suspended solids.

Color

Color is not usually significant in wastewater from electroplating and is indirectly controlled by the effluent limitations on suspended solids and on total metal which controls the amount of colloidal metal that could color the effluent.

Temperature

Temperature is not considered a significant pollution parameter in the electroplating industry. However, cooling water used to cool plating process tanks and/or evaporative recovery systems that are not subsequently used for rinsing could contain pollutants from leaks in the system. Insufficient data exists upon which to base effluent limitations and standards of performance.

SECTION VII

CONTROL AND TREATMENT TECHNOLOGY

Introduction

The control and treatment technology for reducing the discharge of pollutants from copper, nickel, chromium, and zinc electroplating processes is discussed in this section.

The control of electroplating wastewaters includes process modifications, material substitutions, good housekeeping practices, and water conservation techniques. The in-plant control techniques discussed are generally considered to be normal practice in this industry.

The treatment of electroplating wastewaters includes all techniques for the removal of pollutants and all techniques for the concentration of pollutants in the wastewaters for subsequent removal by treatment. Although all of the treatment technologies discussed have been applied to electroplating wastewaters, some may not be considered normal practice in this industry.

Chemical treatment technology is discussed first in this section because treatment of all waste water generated by electroplating is required, prior to water discharge into navigable streams, irrespective of the in-plant controls adopted for reducing waste. Nevertheless, it is emphasized that the amount of pollutants discharged to navigable waters is directly proportional to the volume of water discharged.

The proper design, operation, and maintenance of all wastewater control and treatment systems are considered essential to an effective waste management program. The choice of an optimum wastewater control and treatment strategy for a particular electroplating facility requires an awareness of numerous factors affecting both the quantity of wastewater produced and its amenability to treatment.

Chemical Treatment Technology

Applicability

Chemical treatment processes for waste water from electroplating operations are based on chemical reactions utilized for 25 years or more. A system has evolved that is capable of effectively treating effluents from plants of any size and reducing metal ion concentrations in the effluent to 0.5 mg/liter or less. Control procedures have been devised to maintain the effectiveness of the process under a variety of operating conditions.

Processes

Preceding page blank

Separation of Streams. The rinse waters are usually segregated into three streams prior to treatment, and consist of 1) those containing Cr^{+6}, 2) those containing cyanide, and 3) the remainder, constituting water from acid dips, alkali cleaners, acid copper, nickel, and zinc baths, etc. The cyanide is oxidized by chlorine and Cr^{+6} is reduced to Cr^{+3} with sulfur dioxide or other reducing agents. The three streams are then combined and the metal hydroxides are precipitated by adjustment of the pH. The hydroxides are allowed to settle out, often with the help of coagulating agents, and the sludge is hauled to a lagoon or filtered and used as land fill. The treatment facilities may be engineered for batch, continuous, or integrated operation (7).

Batch Treatment. The batch method is generally used for small or medium-sized plants. Batch treatment is useful not only for rinse waters but for process solutions containing high concentrations of chemicals such as floor spills. Holding tanks collect the wastewater and are large enough to provide ample time to treat, test, and drain a tank while another is being filled. Analytical tests are made before treatment to determine the amount of reagent to add and after treatment to establish that the desired effluent concentrations have been obtained.

Continuous Treatment. The chemical treatment process may be made continuous by (1) sizing and baffling treatment tanks to provide sufficient hold times to complete chemical reactions; (2) providing continuous monitoring of pH and oxidation/reduction potentials and controls for regulating reagent additions by means of these monitors; and (3) providing a continuous-overflow settling tank that allows sludge to be pumped off periodically through the bottom.

A diagram of a continuous-treatment plant operating at maximum capacity is shown in Figure 4. The dilute acid-alkali stream originates from rinses associated with alkaline cleaners, acid dips, and baths containing metal ions but no cyanide or hexavalent chromium. When concentrated acid and alkali baths are to be discarded they are transferred to a holding tank and added slowly to the dilute stream. In this manner, sudden demands on the reagent additions and upsetting of the treatment conditions are avoided. The dilute acid-alkali stream first enters a surge tank to neutralize the wastewater and equalize the composition entering the precipitation tank. The hexavalent chromium is reduced at a pH of 3.5, and the addition of the SO_2 and HCl are controlled by suitable monitors immersed in the well-agitated reduction tank. Cyanide is destroyed in a large tank with compartments to allow a two-stage reaction. Reaction time is about 3 hours.

The treated chrome, cyanide, and neutralized acid- alkali streams are run into a common tank where pH is automatically adjusted to and held at 8.8. The stream then enters a solids contact unit where mixing, coagulation, flocculation, recirculation, solid separation, clarification, solids concentration, sludge

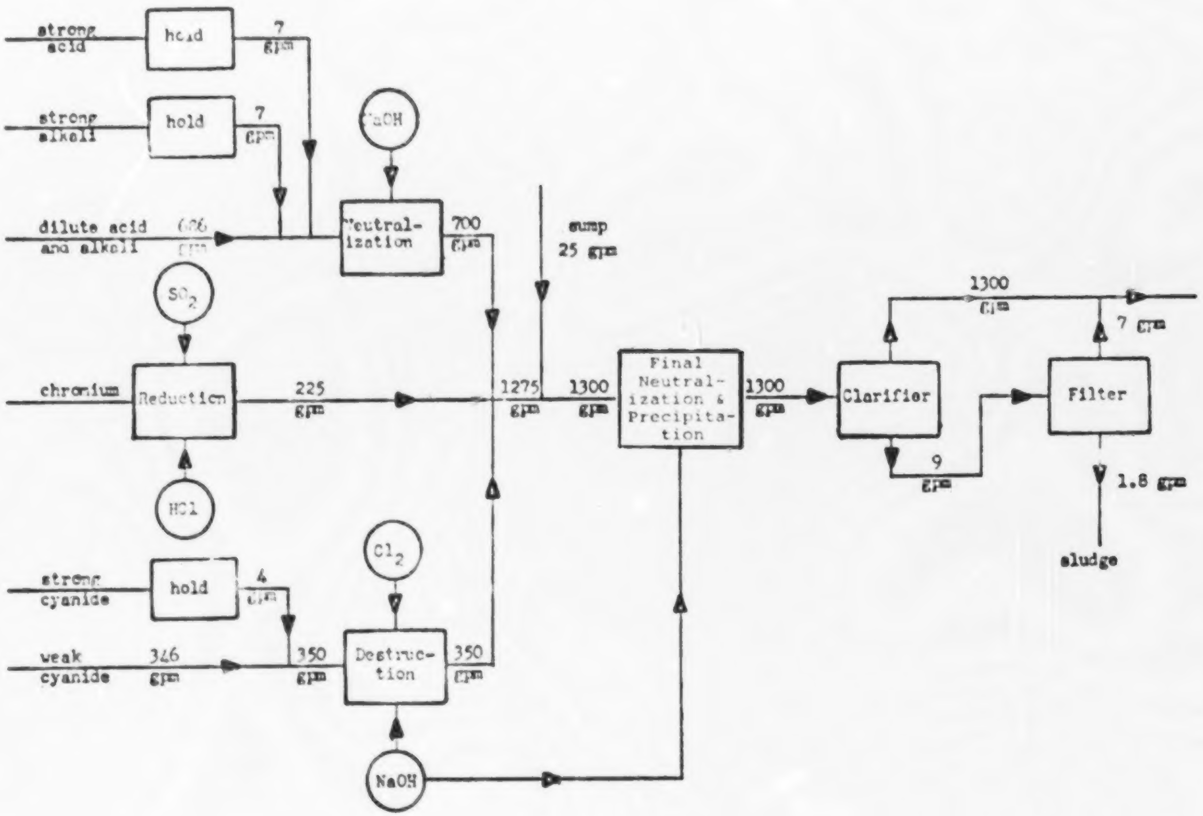

strong acid
hold
7 gpm
strong alkali
hold
7 gpm
dilute acid and alkali
686 gpm
NaOH
Neutral-ization
700 gpm
sump 25 gpm
SO2
chromium
Reduction
225 gpm
HCl
1275 gpm
1300 gpm
Final Neutral-ization & Precipita-tion
1300 gpm
Clarifier
1300 gpm
Filter
7 gpm
9 gpm
1.8 gpm
sludge
strong cyanide
hold
4 gpm
Cl2
weak cyanide
346 gpm
350 gpm
Destruc-tion
350 gpm
NaOH

FIGURE 4. DIAGRAM OF A TYPICAL CONTINUOUS-TREATMENT PLANT

collection, and sludge removal are accomplished. Flocculants are continuously added to this tank. Typically, residence time is 2 hours. The effluent from this tank constitutes the discharge from the plant.

Integrated Treatment. The integrated system uses a reservoir tank in conjunction with the rinse tanks for each type of plating bath. A common solution is circulated through the chemical wash tank (which replaces what is normally the first rinse tank) and the reservoir. The solution contains an excess of treatment chemical so that cyanide destruction takes place in the wash tank and directly on the film of drag-out solution on the part itself. Therefore, no cyanide is dragged into the subsequent rinse tank and no treatment is required for effluent from this tank. Metal hydroxides settle in the reservoir and may be recovered, dissolved, and returned to the plating bath from which they originated. In contrast to batch and continuous treatments, which are generally carried out in a separate facility, the reservoir in the integrated system is in proximity to the plating room because of the necessity for circulation. The layout of an integrated system for treating rinse water waste from a cyanide plating solution and a chromium plating bath is shown in Figure 5.

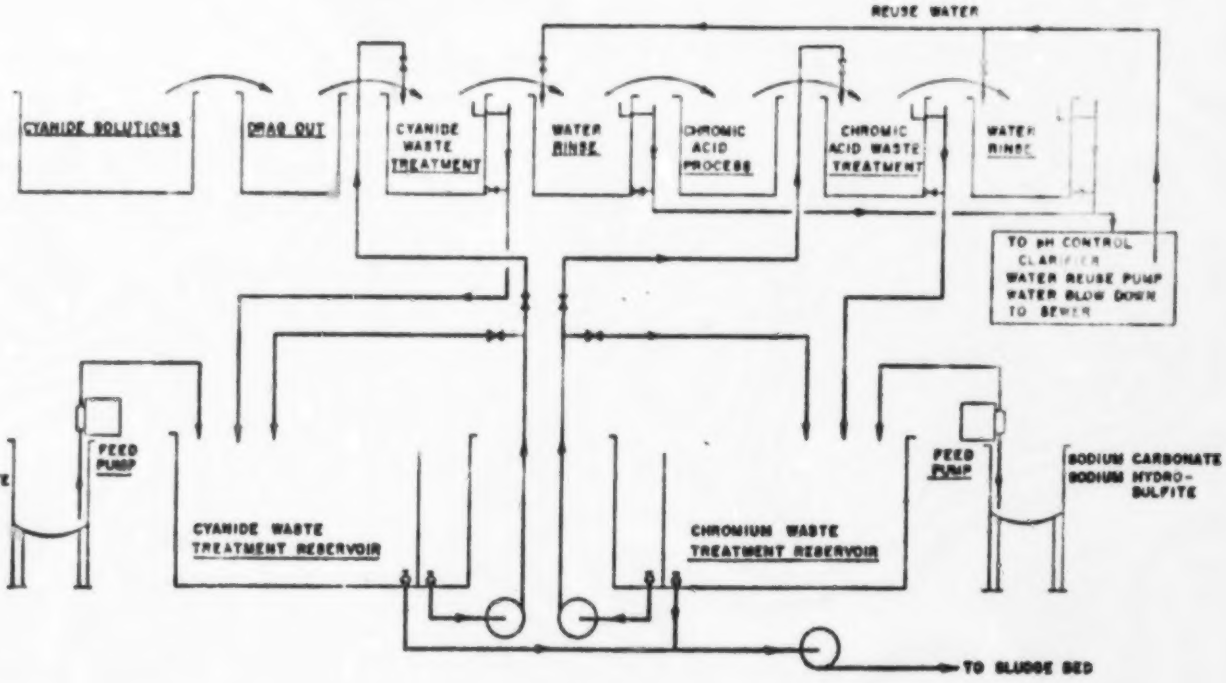

REUSE WATER
CYANIDE SOLUTIONS
DRAG OUT
CYANIDE WASTE TREATMENT
WATER RINSE
CHROMIC ACID PROCESS
CHROMIC ACID WASTE TREATMENT
WATER RINSE
TO pH CONTROL
CLARIFIER
WATER REUSE PUMP
WATER BLOW DOWN
TO SEWER
SODIUM HYPOCHLORITE
FEED PUMP
CYANIDE WASTE TREATMENT RESERVOIR
CHROMIUM WASTE TREATMENT RESERVOIR
FEED PUMP
SODIUM CARBONATE
SODIUM HYDRO-SULFITE
TO SLUDGE BED

FIGURE 5. INTEGRATED TREATMENT SYSTEM

Unit Operations

Precipitation. The effluent levels of metal ions attainable by chemical treatment depend upon the insolubility of metal hydroxides in the treated water and upon the ability to mechanically separate the hydroxides from the process stream. Minimum solubility is attained at a pH in the range of 6 to 9 depending upon the specific conditions present. Effects of coprecipitation and adsorption on the flocculating agents added to aid in settling the precipitate play a significant role in reducing the concentration of the metal ions. Dissolved solids made up of noncommon ions can increase the solubility of the metal hydroxides according to the Debye- Huckel Theory. In a treated solution from a typical electroplating plant, which contained 230 mg/l of sodium sulfate and 1060 mg/l of sodium chloride, the concentration of nickel was 1.63 times its theoretical solubility in pure water. Therefore, salt concentrations up to approximately 1000 ppm should not increase the solubility more than 100 percent as compared to the solubility in pure water. However, dissolved solids concentrations of several thousand ppm could have a marked effect upon the solubility of the hydroxide.

When solubilizing complexing agents are present, the equilibrium constant of the complexing reaction has to be taken into account in determining theoretical solubility with the result that the solubility of the metal is generally increased. Cyanide ions must be destroyed not only because they are toxic but also because they prevent effective precipitation of copper and zinc as hydroxides. If cyanide is replaced in a plating bath by a nontoxic complexing agent such as EDTA (ethylene-diamine-tetraacetic acid), the new complexing agent could have serious consequences upon the removal of metal ions by precipitation.

Solids Separation. The first step in separating the precipitated metals is settling, which is very slow for gel- like zinc hydroxide, but accelerated by coprecipitation with the hydroxides of copper and chromium (10). Coagulation can also be aided by adding metal ions such as ferric iron which forms ferric hydroxide and absorbs some of the other hydroxide, forming a floc. Ferric iron and aluminum sulfate have been used for this purpose in sewage treatment for many years. Ferric chloride is frequently added to the clarifier of chemical waste-treatment plants in plating installations. Flocculation and settling are further improved by use of polyelectrolytes, which are high molecular weight polymers containing several ionizable ions. Due to their ionic character they are capable of swelling in water and adsorbing the metal hydroxide which they carry down during settling.

Settling is accomplished in the batch process in a stagnant tank, and after a time the sludge may be emptied through the bottom and the clear effluent drawn off through the side or top. The continuous system uses a baffled tank such that the stream flows first to the bottom but rises with a decreasing vertical velocity until the floc can settle in a practically stagnant fluid.

Clarifiers are widely used throughout the industry to attain more efficient solids removal. Polishing filters or sand filters may be used on the effluent following clarification to achieve even greater removal.

Sludge Disposal. Clarifier underflow or "sludge" contains typically 1 to 2 percent solids and can be carried to a lagoon. Run-off through porous soil to ground-water is objectionable since precipitated metal hydroxides tend to get into adjacent streams or lakes. Impervious lagoons require evaporation into the atmosphere. However, the average annual rainfall balances atmospheric evaporation. Additionally, heavy rainfalls can fill and overflow the lagoon. Lagooning can be avoided by dewatering the sludge to a semidry or dry condition.

Several devices are available for dewatering sludge. Rotary vacuum filters will concentrate sludge containing 4 to 8 percent solids to 20 to 25 percent solids. Since the effluent concentration of solids is generally less than 4 percent a thickening tank is generally employed between the clarifier and the filter. The filtrate will contain more than the allowed amount of suspended solids, and must, therefore, be sent back to the clarifier.

Centrifuges will also thicken sludges to the above range of consistency and have the advantage of using less floor space. The effluent contains at least 10 percent solids and is returned to the clarifier.

Pressure filters may be used. In contrast to rotary filters and centrifuges, pressure filters will produce a filtrate with less than 3 mg/l of suspended solids so that return to the clarifier is not needed. The filter cake contains approximately 20 to 25 percent solids. Pressure filters are usually designed for a filtration rate of 2.04 to 2.44 liters/min/sq m (0.05 to 0.06 gpm/sq ft) of clarifier sludge.

Solids contents from 25 to 35 percent in filter cakes can be achieved with semi-continuous tank filters rated at 10.19 to 13.44 liters/min/sq m (0.25 to 0.33 gpm/sq ft) surface. A solids content of less than 3 mg/l is normally accepted for direct effluent discharge. The units require minimum floor space.

Plate and frame presses produce filter cakes with 40 to 50 percent dry solids and a filtrate with less than 5 mg/l total suspended solids. Because automation of these presses is difficult, labor costs tend to be high. The operating costs are partially off-set by low capital equipment costs.

Automated tank type pressure filters are just now finding application. The solids content of the cake can be as high as 60 percent while the filtrate may have up to 5 mg/l of total suspended solids. The filtration rate is approximately 2.04 liters/min/sq m (0.05 gpm/sq ft) filter surface area. Pressure filters can also be used directly for neutralized wastes containing from 300 to 500 mg/l suspended solids at design rates of 4.88 to 6.52 liters/min/sq m (0.12 to 0.16 gpm/sq ft) and still maintain a low solids content in the filtrate.

Filter cakes can easily be collected in solid waste containers and hauled away to land fills. There may be situations, however, where the metal in the filter cake could redissolve if it came into contact with acidic water. Careful consideration should be given to where such a material is dumped.

Several companies have developed proprietary chemical fixation processes which are being used to solidify sludges prior to land disposal. In contrast to filtration, the amount of dried sludge to be hauled away is increased. Claims are that the process produces insoluble metal ions so that in leaching tests only a fraction of a part per million is found in solution. However, much information is lacking on the long term behavior of the "fixed" product, and potential leachate problems which might arise. The leachate test data and historical information to date indicate that the process has been successfully applied in the disposal of polyvalent metal ions and it apparently does have advantages in producing easier to handle materials and in eliminating free water. Utilization of the chemical fixation process is felt to be an improvement over many of the environmentally unacceptable disposal methods now in commong usage by industry. Nevertheless, chemically fixed wastes should be regarded as easier to handle equivalents of the raw wastes and the same precautions and requirements required for proper landfilling of raw waste sludges should be applied.

The possibility of recovering metal values from sludges containing copper, nickel, chrome, and zinc has been considered(12) but such a system appears to be uneconomic under present circumstances. It may be profitable to recover metal values if 900 to 2300 kg (2,000 to 5,000 pounds) of dried sludge solids can be processed per day with a thoroughly developed process. To attain this capacity would almost certainly require that sludge from a large number of plants be brought to a central processing station. The recovery would be simpler if the metallic precipitates were segregated, but segregation would require extensive modifications, investment, and increased operating expense for precipitation and clarification. Laboratory experiments showed that zinc could be leached from sludge with caustic after which copper, nickel, and chromium were effectively dissolved with mineral acids. Ammonium carbonate dissolved copper and nickel but not trivalent chromium, thus giving a method of separation. Electrowinning of the nickel and copper appeared to be a feasible method of recovering these metals.

Practical Operating Systems. Relatively few plating installations have installed filters, although the problems of disposing of unfiltered sludge should provide an impetus for use of more filters in the future. Plant 12-8 has a large rotary filter in routine operation, and the practicality of this unit has been well established. The Chemfix system is in use at several plants.

Demonstration Status. Centrifuges are used for dewatering sludge in the new waste treatment facility at Rock Island Arsenal. Since the whole waste treatment system at Rock Island has not yet been operated on a continuous basis the feasibility of the concepts and the components used remains to be demonstrated.

Cyanide Oxidation. Cyanide in wastewaters is commonly destroyed by oxidation with chlorine or hypochlorite prior to precipitation of the metal hydroxides. The method is simple, effective, and economically feasible even for small volume installations. A comprehensive study of the method was made by Dodge and Zabban (10-13), the results of which have been used to work out the practical processes. The following are proposed reactions for chlorine oxidation:

(1) $NaCN + Cl_2 \rightarrow CNCl + NaCl$

(2) $CNCl + 2NaOH \rightarrow NaCNO + NaCl + H_2O$

(3) $2NaCNO + 3Cl_2 + 4NaOH \rightarrow N_2 + 2CO_2 + 6NaCl + 2H_2O.$

Reaction (2) goes rapidly at pH 11.5, under which conditions, build up of the toxic gas CNCl by Reaction (1) is avoided. Treatment of dilute rather than concentrated solutions also minimizes its formation. Oxidation to cyanate (NaCNO) is completed in 5 minutes or less. Reaction (3) goes more slowly, requiring an hour in the preferred pH range of 7.5 to 9.0, and a longer time at higher pH. After the conversion to nitrogen and carbon dioxide, excess chlorine is destroyed with sulfite or thiosulfate.

Sodium hypochlorite may be used in place of chlorine. Recent technical innovations in electrochemical hypochlorite generators for on-site use raise the possibility of controlling the addition of hypochlorite to the cyanide solution by controlling the current to the electrochemical generator, using sodium chloride as the feed material.

Concentrated solutions, such as contaminated or spent baths, cyanide dips, stripping solutions, and highly concentrated rinses, are normally fed at a slow rate into a dilute cyanide stream and treated with chlorine. However, concentrated solutions may also be destroyed by electrolysis with conventional equipment available in the plating shop (18). In normal industrial practice the process is operated batchwise, whereas the optimum system, from an operating standpoint, would be a cascaded one in which successively larger tanks are operated at successively lower current densities. This is the more efficient system. In addition to the oxidation of cyanide at the anode, valuable metal can be recovered at the cathode. The process becomes very inefficient when the cyanide concentration reaches 10 ppm, but at this point the solution can be fed into the process stream for chemical destruction of cyanide to bring the concentration to the desired level. The addition of chloride ions to the concentrated solutions, followed by electrolysis, produces chlorine or hypochlorite in solution, which can then destroy the cyanide to the same low levels as obtained by direct chlorination. With the provision that chlorine or hypochlorite be formed at a rate equal to the concentration of cyanide passing through the system, the process can be operated continuously:

$$2NaCN + 2NaOCl \longrightarrow 2NaCNO + 2NaCl$$

$$2NaCNO_3 + 3NaOCl + H_2O \longrightarrow 2CO_2 + N_2 + 2NaOH + 3NaCl$$

$$2NaCN + 5NaOCl + H_2O \longrightarrow 2CO_2 + N_2 + 2NaOH + 5NaCl.$$

One proprietary process (A), based on the above principles, claims to produce 1 kg of active chlorine per 5.5 KwH (19). Equipment needs are the same with the exception that the tanks must be lined and graphite or platimized anodes must be used.

Polysulfide-cyanide strip solutions containing copper and nickel do not decompose as readily and as completely as do plating solutions. Although the cyanide content can be reduced from 75,000 to 1000 mg/l during two weeks of electrolysis anode scaling prevents further cyanide decomposition unless anodes are replaced or freed from scale. Minimum cyanide concentration attainable is about 10 mg/l after which the solution can be treated chemically.

The electrolysis of dilute cyanide solution can be improved by increasing the electrode area. Area can be increased by filling the space between flat electrodes with carbonaceous particles (20). The carbon particles accelerate the destruction process 1000 times, but flow rate through the unit must be carefully adjusted, if used on a continuous basis to achieve complete destruction (Plant 30-1).

Although cyanide can be destroyed by oxygen or air under suitable conditions (21,22), cyanide concentrations in the effluent are reported to be 1.3 to 2.2 mg/l, which is high for discharge to sewers or streams. A catalytic oxidation unit using copper cyanide as a catalyst and activated carbon as the reactive surface has been described for oxidizing cyanide with air or oxygen (23), and at least two units were put in operation. The most recent information on these units is that they are not operating and that at present the units are not being sold.

Ozone will oxidize cyanide (to cyanate) to below detectable limits independent of the starting concentration or of the complex form of the cyanide(24,25,26). The reaction can be completed even with the very stable iron complexes if heat or ultraviolet light is used in conjunction with the ozone. The potential advantages of ozone oxidation are enhanced by the efficiency and reliability of modern ozone generators, and development work is continuing.

A method employing thermal decomposition for cyanide destruction has been recently announced (27). Cyanide solution is heated to 160 to 200 C under pressure for 5 to 10 minutes. Ammonia and formate salts are formed. No information is given on the final cyanide concentration.

Another proprietary process (B) claims to destroy cyanides of sodium, potassium, zinc, and cadmium and also precipitates zinc and cadmium. The process is discussed later in this section.

Precipitation of cyanide as ferrocyanide is restricted to concentrated wastes. Ferrocyanide is less toxic than cyanide, but is converted back to cyanide in sunlight. Treatment is accomplished by adding an amount in excess of stoichiometry (2.3 kg of $FeSO_4$ per kg of cyanide). Large amounts of sludge are produced which add to the pollution load. Complex cyanides do not break down readily and the reaction stops when a concentration of 10 mg/l of cyanide is reached. No benefits can be foreseen in terms of reducing waste volume and concentration.

Cyanide is also destroyed by reaction with polysulfides. Reasonable reaction rates are obtained only if the solution is boiled. Since the reaction does not destroy all of the cyanide further treatment is necessary.

For a small electroplating facility, it is conceivable that an electrodialysis system for the distruction of cyanide could be installed. Experimental work has been performed on copper cyanide plating baths and is applicable to cyanide baths of zinc, cadmium, silver, and gold.

Reduction of Hexavalent Chromium. Hexavalent chromium (Cr^{+6}) is usually reduced to trivalent chromium at a pH of 2 to 3 with sulfur dioxide (SO_2), sodium bisulfite, other sulfite-containing compounds, or ferrous sulfate. The reduction makes possible the removal of chromium as the trivalent hydroxide which precipitates under alkaline conditions. Typical reactions for SO_2 reduction are as follows:

$$SO_2 + H_2O \longrightarrow H_2SO_3$$

$$2H_2CO_4 + 3H_2SO_3 \longrightarrow Cr_2(SO_4)_3 + 5H_2O.$$

Representative reactions for reduction of hexavalent chromium under acidic conditions using sulfite chemicals instead of SO_2 are shown below:

(a) Using sodium metabisulfite with sulfuric acid:

$$4H_2CrO_4 + 3Na_2S_2O_5 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2Cr_2(SO_4)_3 + 7H_2O$$

(b) Using sodium bisulfite with sulfuric acid:

$$4H_2CrO_4 + 6NaHSO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + 2Cr_2(SO_4)3 + 10H_2O$$

(c) Using sodium sulfite with sulfuric acid:

$$2H_2CrO_4 + 3Na_2SO_3 + 3H_2SO_4 \longrightarrow 3Na_2SO_4 + Cr_2(SO_4)_3 + 5H_2O.$$

Reduction using sulfur dioxide is the most widely used method, especially with larger installations. The overall reduction is readily controlled by automatic pH and ORP (oxidation-reduction potential) instruments. Treatment can be carried out on either a continuous or batch basis.

Hexavalent chromium can also be reduced to trivalent chromium in an alkaline environment using sodium hydrosulfite as follows:

$$2H_2CrO_4 + 3N_2H_2 \xrightarrow{Na_2CO_3} 2Cr(OH)_3 + 3N_2 + 2H_2O.$$

As indicated in the above equation, the chromium is both reduced and precipitated in this one-step operation. Results similar to those obtained with sodium hydrosulfite can be achieved using hydrazine under alkaline conditions.

$$2H_2CrO_4 + 3N_2H_2 \xrightarrow{Na_2CO_3} 2Cr(OH)_3 + 3N_2 + 2H_2O.$$

Sodium hydrosulfite or hydrazine are frequently employed in the precipitation step of the integrated system to insure the complete reduction of any hexavalent chromium that might have been brought over from the prior reduction step employing sulfur dioxide or sodium bisulfite. Where ferrous sulfate is readily available (e.g., from steel pickling operations), it can be used for reduction of hexavalent chromium; the reaction is as follows:

$$2CrO_3 + 6FeSO_4 \cdot 7H_2O + 6H_2SO_4 \longrightarrow 3Fe_2(SO_4)_3 + Cr_2(SO_4)_3 + 13H_2O.$$

Cr^{+6} may be reduced at a pH as high as 8.5 with a proprietary compound (28). It is not necessary to segregate chromate-containing wastewaters from the acid-alkali stream, and the use of acid to lower pH is eliminated in this case. Precipitation of chromic hydroxide occurs simultaneously in this case with the reduction.

chromic hydroxide occurs simultaneously in this case with the reduction.

Cr^{+6} ions may be reduced electrochemically.(26) concentration of 100 mg/l was reduced to less than 1 mg/l with a power consumption of 1.2 kwh/1,000 liters. The carbon bed electrolytic process previously described for cyanide(24) may also be used for chromate reduction in acid solution and Plant 30-1 has achieved a Cr+6 concentration of .01 mg/l using this method. Electrolysis may also be used to regenerate a reducing agent. A process(27) has been described involving the reduction of Fe(III) to Fe(II) electrochemically and the reduction of Cr^{+6} by Fe(II). The method should be capable of achieving low Cr^{+6} levels.

The simultaneous reduction of Cr^{+6} and oxidative destruction of cyanide finds limited application in waste-treatment practice. The reaction requires mixing of Cr^{+6} and CN in ratios between 2 and 3 using Cu^{+2} as a catalyst in concentrations of 50 to 100 mg/l. The catalyst introduces additional pollutant into the waste stream. Reaction rates are generally slow, requiring from 6 to 24 hours for cyanide concentrations ranging from 2,000 to less than 50 mg/l at a solution pH of 5. The slowness of the reaction and the high initial concentrations of reactants required may make the method unsuitable for treating rinse waters. Its use is limited to batch treatment of concentrated solutions. No benefits are obtained in terms of water volume and pollution reduction. Destruction is not as complete as obtained by the more common chemical methods.

Practical Operating Systems

Chemical treatment is used by every plant contacted during the effluent guidelines study with the exception of those that are allowed to discharge plating waste effluents into sewers or streams without treatment.

The effectiveness of chemical treatment techniques depends on the nature of the pollutant, the nature and concentration of interfering ions, the procedure of adding the appropriate amount of chemicals (or adjusting pH), the reaction time and temperature and the achievement of effective separation of precipitated solids. The concentration of an individual pollutant in the solution being treated has no effect on its final concentration after treatment. On the other hand, effective removal of heavy metal pollutants is inhibited by some types of chelating ions such as tartrate or ethylene diamine tetracetate ions.

The concentrations of metals and cyanide achievable by the chemical techniques employed for treating waste from copper, nickel, chromium, and zinc electroplating and zinc chromating processes are summarized in Table 20. Concentrations lower than those listed as maximum in Table 20 were reported by companies using all three (continuous, batch, and integrated) treating systems. The data show that the soluble concentration levels

TABLE 20 CONCENTRATIONS OF HEAVY METALS AND CYANIDE ACHIEVABLE BY CHEMICAL TREATING OF WASTE CREATED BY COPPER, NICKEL, CHROMIUM AND ZINC PLATING AND ZINC CHROMATING OPERATIONS

Pollutant	Soluble Concentration After Chemical Treating		Contribution From Suspended Solids[(2)]	
	Minimum, mg/ℓ	Maximum, mg/ℓ[(1)]	Minimum, mg/ℓ	Maximum, mg/ℓ
Cyanide, oxidizable[(3)]	< 0.01	0.03	--	--
Cyanide, total	0.1	0.2	--	--
Phosphorus	0.007	0.6	--	--
Chromium 6+	< 0.01	0.05	--	--
Chromium, total	0.05	0.25	0.02	0.30
Copper	< 0.01	0.2	0.02	0.76
Nickel	< 0.01	0.5	0.02	0.15
Zinc	0.05	0.5	0.04	0.80
Total suspended solids[(2)]	20.	24.		

(1) Values below these limits have been reported by plants utilizing continuous (Plants 40-6, 8-4, 33-6, and 11-8), batch (Plants 36-1, 21-3, and 33-8) and integrated (Plants 36-2 and 20-13) treatment techniques. Others (Plants 3-3 and 33-3) utilize a combination of integrated and batch or continuous treatments to achieve these or lower limits.

(2) Data for Plants 33-1, 12-8, 36-1 and 11-8 .

(3) Oxidizable by chlorine.

achieved in practice are near those that would be expected based on solubility data discussed previously.

Higher-than-normal concentrations of copper, nickel, chromium, and zinc, when they occur, are usually caused by: (1) inaccurate pH adjustment (sometimes due to faulty instrument calibration); (2) insufficient reaction time: or (3) excessive concentrations of chelating agents that complex the metal ions and prevent their reaction with hydroxyl ions to form the insoluble metal hydrates. The causes for higher-than-normal concentrations of cyanide are similar, but another important factor must be added to the list of potential causes for incomplete cyanide destruction. In this case, sodium hydroxide and chlorine must be added and provide sufficient reagent to complete the reaction, which is normally monitored by an oxidation-reduction-potential (ORP) recorder-controller. The maintenance of this system is a critical factor affecting the effectiveness of chemical oxidation.

Suspended Solids. The suspended solids discharged after treatment and clarification sometimes contribute more copper, chromium, and zinc than the soluble metal concentrations, as shown in Table 20. For example, the copper contribution from the total suspended solids determined for four plants engaged in copper, nickel, chromium, and zinc electroplating was in the range of 0.02 to 0.76 mg/l. Zinc contributions from suspended solids ranged from 0.03 to 0.80 mg/l. The total copper, nickel, chromium, and zinc content in suspended solids was equivalent to as much as 2.04 mg/l, in comparison with a maximum of 1.45 mg/l for these metals in the soluble form.

The concentration of total suspended solids in the end-of-pipe discharge from typical chemical treatment operations ranged from 20 to 24 mg/l. Maintaining conditions so as not to exceed these amounts requires (1) a properly designed settling and/or clarifying facility, (2) effective use of flocculating agents, (3) careful removal of settled solids, and (4) sufficient retention time for settling. Of course, minimum retention time depends on the facility size and In practice, this time ranges from about 2 to 8 hours for plants that are able to reduce suspended solids to about 25 mg/l. Even so, this achievement requires very good control of feeding flocculating agents.

Precipitation of Metal Sulfides

Applicability. The sulfides of copper, nickel, and zinc are much less soluble than their corresponding hydroxides.

Precipitation using hydrogen sulfide or soluble sulfides (Na_2S) involves toxicity problems with the excess reagent used. However, a system has recently been developed that provides for sulfide precipitation without the toxicity problems.(31) It should be applicable to treatment of effluent from electroplating operations.

Process Principles and Equipment

Ferrous sulfide, which has a higher solubility than the sulfides of the metals to be precipitated is used as the precipitating reagent. However, the solubility of ferrous sulfide is still so small (5-10 mg/l of sulfide ion) that the toxicity problem is eliminated. Freshly precipitated ferrous sulfide is most reactive and is obtained by adding an excess of a soluble sulfide for precipitating the metals to be removed from the effluent and then adding sufficient soluble ferrous salt to precipitate all excess sulfide ion. The pH is normally adjusted to the range of 7 to 8, prior to precipitation. Hexavalent chromium that may be present is reduced to Cr^{+3} by the ferrous iron and immediately precipitated as the hydroxide. Therefore, no extra precipitation steps are necessary to remove the chromium. If the extra ferrous ions in solution are considered undesirable they may be oxidized to Fe(III) which will precipitate as the hydroxide. However, removal of iron would not be possible until after the sulfide precipitates had been separated from the liquid. In principle, it should be possible to precipitate metallic sulfides from metal ion complexes that are not amenable to chemical treatment by hydroxide precipitation, due to the lower solubilities of the sulfides. It has been demonstrated that copper can be effectively precipitated from the ammonia complex.

Demonstration Status

The process described is in development stage and it is anticipated that a demonstration plant will be built and operated in the near future.

Combined Metal Precipitation and Cyanide Destruction - Proprietary Process B

Applicability. This proprietary process (32) is applicable to zinc and cadmium cyanide solutions. The metal hydroxide is precipitated and cyanide is decomposed. Applicability depends upon deciding whether the products of cyanide decomposition are suitable for discharge or not. The effluent is considered suitable for discharge to sewers in some states and may be acceptable in certain areas for discharge to streams. A modified process may be applicable to copper cyanide.

Process Principles and Equipment

Cyanide in zinc and cadmium plating baths is destroyed by a mixture of formalin and hydrogen peroxide according to the formula:

$CN^- + HCOH + H_2O_2 + H_2O \longrightarrow CNO^- + NH_4 + H_2C(OH)COHN_2$ glycolic acid amide.

The metal hydroxide is also precipitated. The hydrogen peroxide is contained in the reagent (41%) which contains stabilizers and additives to promote the reactions and help in settling the metal hydroxide precipitate. The process may be carried out on a batch or continuous basis, and is particularly convenient for the small shop. Figure 6 shows the apparatus for batch treatment. To be economical the rinse water should contain at least 55 ppm of cyanide, and sufficient counter-flow rinses are normally installed to assure a sufficient cyanide concentration. The typical treated effluent contains 0.1 mg/l of cyanide and 1 to 2 mg/l of zinc. Table 21 shows an analysis of the products for decomposing 794 ppm of cyanide.

Practical Operating Systems. This process is well established as a practical means for pollution control and is being used in approximately 30 installations.

Water Conservation Through Control Technology

The volume of effluent is reduced if water is conserved during rinsing operations. The solubility limit of effluent constituents is essentially constant, so that a reduction in the effluent volume accomplishes a reduction in the amount of effluent constituents discharged. Water conservation can be accomplished by in-plant process modifications requiring little capital or new equipment, materials substitutions, and good housekeeping practice. Further water conservation is obtained by installing counterflow rinse tanks and ion-exchange, evaporative recovery, or reverse osmosis systems. Other systems that may accomplish water conservation are freezing, electrodialysis, electrolytic stripping, carbon adsorption, and liquid-liquid extraction.

Process Modifications

Wastes from electroplating operations can sometimes by reduced by the following changes in electroplating processes:

(1) Elimination of copper prior to nickel and chromium plating, especially for plating on steel

(2) Elimination of copper by increasing the thickness of nickel

(3) Substitution of a nickel strike for a copper strike and replacing the highrate copper cyanide solution with a copper sulfate bath

(4) Substitution of low-concentration electroplating solutions for high concentration baths.

Metals remaining in solution after chemical treatment of the effluent from a plant plating decorative copper, nickel, and

TABLE 21. DECOMPOSITION PRODUCTS OF CYANIDE IN RINSE WATER(1) FROM A CYANIDE ZINC ELECTROPLATING OPERATION AFTER TREATMENT WITH PEROXYGEN COMPOUND

Products Formed by Treatment	Amount Formed		
	Actual	Cyanide Equivalent	
	ppm	ppm	percent
Cyanate	351	265	33
Ammonia (free)			
Dissolved	57	164	21
Volatilized	32	91	11
Combined Ammonia			
Calc'd as NH_3	95		
Calc'd as glycolic acid amide	419	274	35
		794	100

(1) Analysis of water before treatment:

Cyanide	794 ppm
Cyanate[2]	336 ppm
Ammonia[2]	41 ppm.

Cyanide calculated as NaCN, cyanate as NaOCN, and ammonia as NH_3.

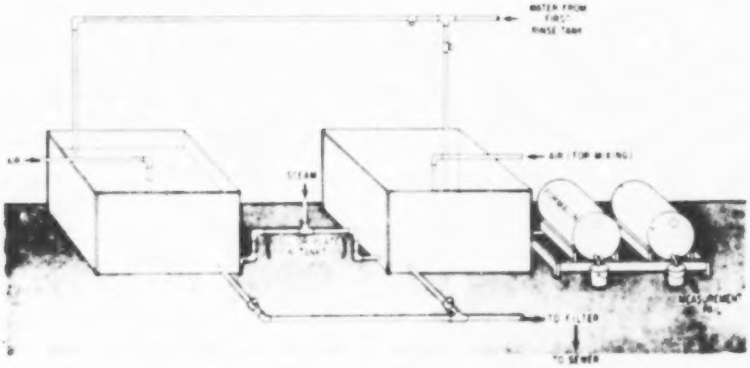

WATER FROM FIRST RINSE TANK
AIR
STEAM
AIR (FOR MIXING)
MEASUREMENT
TO FILTER
TO SEWER

FIGURE 6. BATCH TREATMENT OF CYANIDE RINSE WATERS BY COMBINED METAL PRECIPITATION AND CYANIDE DESTRUCTION

chromium can be reduced in amount by eliminating the copper. Some steel products can be plated directly with nickel and chromium, especially when the quality of the steel surface is improved. A better grade of steel or a change in mechanical finishing methods to reduce surface roughness can sometimes justify the elimination of copper without sacrificing high specularity. To maintain good corrosion resistance on steel products and eliminate copper, it may be necessary to increase the thickness of the nickel or install duplex nickel in place of bright nickel, which is much better than a single layer of bright nickel for providing maximum corrosion resistance. To maintain a high degree of specularity in the absence of a copper plate, leveling nickel is recommended.

The substitution of a nickel strike for a copper strike has been adopted in several plants plating nickel and chromium on steel. A copper sulfate solution is then utilized after nickel striking in some cases. This change avoids copper cyanide baths and the attendant need for oxidizing cyanide in the treatment system and has been particularly successful for steel products.

Substitution of low-concentration electroplating solutions for high-concentration baths has been adopted in recent years, principally for reducing the cost of chemicals used for cyanide destruction. The dilute solutions require less water for rinsing when electroplated parts are transferred to rinse tanks. Assuming a 50 percent reduction in total dissolved solids in the plating solution and two rinse tanks in series, a 30 percent reduction in rinse water requirements is achieved. Wastewater constituents requiring treatment are reduced by the same amount. Adverse effects in terms of lower efficiency and reduced productivity per unit facility may be encountered when dilution is adopted to conserve rinse water and reduce wastewater constituents requiring treatment, unless other factors affecting plating rate are modified to adjust for the effects of dilution. Thus, dilution should not be adopted before a complete analysis is made of all pertinent factors.

The advent of effluent limitations is expected to encourage research and development on other processes that will eliminate or reduce water waste. A dry process for applying chromate coatings, which is currently being developed, may prove useful for such a purpose. Chemical vapor deposition processes partially developed a few years ago may be revived for plating hard chromium.

Materials Substitutions

Noncyanide solutions, which have been developed for copper and zinc in place of cyanide solutions, reduce the costs of treatment by eliminating cyanide destruction, but do not eliminate treatment to precipitate and separate the metals. The chelating agents employed in some noncyanide baths to keep the metal in soluble form are precipitated when rinse water waste is treated with lime to precipitate the metals, but other agents such as ethylene diamine tetraacetic acid inhibit the precipitation of zinc and contribute organic matter to the treated water waste. Thus, the applicability of the noncyanide solutions as replacements for cyanide baths must be considered carefully in the light of the effluent limitation guidelines recommended in this document.

Trivalent chromium baths have recently been introduced to the electroplating industry. They eliminate the need for sulfur dioxide reduction of wastewater associated with chromium plating. The trivalent chromium baths appear to have other advantages for decorative plating such as better throwing power, current efficiency and plating rate. The dark color of the deposits is cited as a disadvantage by some purchasers, however. Nevertheless, this process modification may ultimately prove to be significant for reducing waste treatment costs. No details have been released on the treatment required for minimizing the soluble chromium concentration in treated effluent.

Good Housekeeping Practices

Good housekeeping practices that reduce the waste generated in electroplating facilities include the following:

(1) Maintain racks and rack coatings to prevent the transfer of chemicals from one operation to another. (Loose rack coatings are noteworthy as an example of poor practice.)

(2) Avoid overcrowding parts on a rack, which inhibits drainage when parts are removed from a process solution.

(3) Plug all floor exits to the sewer and contain spills in segregated curbed areas or trenches, which can be drained to direct the spills to rinse water effluent with the same chemicals.

(4) Wash all filters, pumps and other auxillary equipmentin curbed areas or trenches, which can be drained to direct the wash water to a compatible holding tank or rinse water stream.

(5) Install anti-syphon devices on all inlet water lines to process tanks.

(6) Inspect and maintain heating and cooling coils to avoid leaks.

(7) Inspect and maintain all piping installed for wastewater flow, including piping from fume scrubbers.

Water Conservation by Reducing Dragout

Dragout. Dragout is defined as solution on the workpiece carried beyond the edge of the plating tank. The dragout of concentrated solution from the plating tank can vary over a wide range depending on the shape factor of the part. A value of 16.3 liters/1000 sq m (0.4 gal/1000 sq ft)(33) is considered a minimum for vertical parts that are well drained. The practical range for parts of various shapes that are well drained is about 40 to 400 liters/sq m (1 to 10 gal/1000 sq ft).

Dragout Reduction. Water used for rinsing can be conserved by (1) improving the racking procedure to improve drainage from surfaces over the process tank, prior to transfer to the subsequent rinse tank, (2) increasing the drainage time over the process tank, (3) reducing the viscosity of the process solution by diluting it or increasing its temperature, (4) adding a wetting agent to the process solution to reduce surface tension, (5) installing fog nozzles above the process tank to return a part of the solution remaining on work surfaces to the process solution, and (6) installing a drip-save (reclaim) tank between the process and rinse stations to collect dragout that is pumped back to the process solution. A mixture of air and water is utilized in one version of a fog nozzle claimed to be especially effective for removing most of the solution from surfaces lifted above process tanks. With the above techniques, the water needed for rinsing can be reduced as much as 50 to 60 percent. Detailed comments on these dragout reduction techniques appear in Reference 34.

Reduction of dragout with the above methods is not without problems. By returning chemicals to the plating tank, impurities tend to build up in the plating solution. Therefore, purification systems, such as ion exchange, batch-chemical treatments, and/or electrolytic purification are required to control impurities. The purification systems create some effluents which must be treated prior to end-of-pipe discharge.

Water Conservation During Rinsing

When effective chemical treatment exists, reduction in pollutional load can be accomplished by reducing the water use in the facility. The principal water use is for rinsing. Use of only that water needed for effective rinsing based on dissolved solids would represent good practice.

Water conservation procedures that are used after processed work is transferred to a rinse tank include (1) adding a wetting agent to the rinse water, (2) installing air or ultrasonic agitation and (3) installing counterflow rinses whereby water exiting the last tank in the rinsing operation becomes feed water for the preceding rinse. With two counterflow rinses, water consumption is reduced 96 percent in comparison with a single rinse, with equivalent rinsing effectiveness. Use of conductivity meters in the final rinse provides automatic control of water use according to need. Rinse water flow is shut off automatically when no work is being processed. Excessive use of water can also be avoided by use of flow restrictors in the water feed lines.

Although multitank, counterflow rinsing imposes capital investment costs for tanks, pumps, and floor space, these costs are compensated by a savings in water (and sewer) charges. Further incentive is provided when regulatory agencies require pollutional control. When end-of-process chemical treatment is used, design of wastetreatment facilities usually indicates the economic advantage of reducing rinse-water flow by installing two or more counterflow rinses.

Because waste-treatment facilities are usually over- designed to handle future expansion in production, there is a tendency to use the water flow capacity of the treatment facility whether or not it is needed for effective rinsing. Furthermore, rinse water flows set by an orifice are not always turned off when plating production is shut down. In the case of an overdesigned installation, it is probably more economical to reduce rinse water usage by use of good rinsing practice than to increase water-treatment facilities in the event of an increase in production.

Rinsing can be carried out beyond the point consistent with good practice, even though there is an economic incentive to save water. The result is unnecessary pollution. Typical concentration levels permitted in the rinses following various process tanks, should not be decreased unless definite quality problems can be associated with the dissolved solids concentrations listed below for representative rinsing systems: (35)

Process	Max Dissolved Solids in Final Rinse, mg/l
Alkaline cleaners	750
Acid cleaners, dips	750
Cyanide plating	37
Copper plating	37
Chromium plating	15
Nickel plating	37
Chromium bright dip	15
Chromate passivating	350-750

A Watts-type plating bath typically contains 270,000 mg/l of total dissolved solids. Obtaining 37 mg/l in the final rinse requires 27,600 liters (7300 gallons) of rinse water if a single rinse tank is used, in order to dilute 3.78 liters (1 gallon) of a Watts-type plating solution containing 270 g/l of dissolved solids. The same degree of dilution in a final rinse tank may be obtained with less water by use of series and counterflow arrangement of two or more rinse tanks. If the tanks are arranged in series and fresh water is fed in parallel to each tank in equal volume, the ratio, r of rinse water to dragout is:

$$r = (CO/CF)\ 1/n$$

where Co = concentration in the process solution CF = concentration in last rinse tank and n = number of rinse tanks.

If the tanks are arranged in the same way but flow proceeds from the last rinse tank to the first rinse tank (counterflow),

$$r = (CO/CF)^{1/n}$$

By feeding water to counterflow tanks instead of in series, the reduction in water varies n-fold. Values of n calculated for several rinsing combinations, using the Co and CF values given above for a nickel bath are as follows:

Rinse Combination	Rinse Ratio, r
Single rinse	7300
Two rinses, parallel feed	171
Three rinses, parallel feed	58.3
Two rinses, counterflow feed	85.5
Three rinses, counterflow feed	19.5

There is a significant reduction in water use by addition of a second rinse tank, and at least two rinse tanks can be considered normal practice. These should best be fed in counterflow. Counterflow rinse tanks increase the concentration of a metal or another constituent in the first rinse tank following the plating or process bath. The water in the first rinse tank can be used to supply make-up water for the plating bath. As the concentration in the first rinse tank increases, more of the drag-out from the plating bath can be returned to the bath in the make-up water, and less will require treatment and/or disposal. Therefore, the addition of countercurrent rinse tanks can decrease both the volume of water to be treated and the amount of dissolved metal that must be removed, at least in some cases.

The rate of evaporation from the plating bath is a factor in determining how much make-up water must be added. Operating a bath at a higher temperature will allow more of the drag-out to be returned to the bath because of the higher rate of evaporation. However, the temperature at which a bath may be operated is sometimes limited because of the decomposition of bath components. Progress has been made in developing bath components that allow higher bath temperatures to be used. For example, brighteners for zinc cyanide baths have been developed(36) which allow bath operation at 50°C (120°F) as compared to 32°C (90°F) for baths using older aldehyde-type brighteners. Thus, the new brighteners permit the return of more of the dragout to the plating bath and a lessened load on the waste treatment system, in addition to what other processing advantages they may offer.

Water Conservation by Ion Exchange

Applicability. Ion exchange is currently a practical commercially accepted method for the in-process treatment of (1) raw water, (2) plating baths, and (3) rinse waters. Raw water is treated to provide de-ionized water for both makeup and critical final rinsing operations. Plating baths are treated to remove impurities, i.e., removal of nickel ions from a chromic acid bath with a cation exchange resin. Rinse waters are treated to provide water that can be returned to the process solution. The concentrated regenerant can be chemically treated more easily than the original volume of rinse water and in some cases the chemicals can be recovered and returned to the bath. The in-process treatment of chromium and nickel plating effluents by ion-exchange techniques are the more economically attractive treatment operations currently being carried out. Ion exchange also is beginning to find increased use in combination with evaporative and reverse-osmosis systems for the processing of electroplating rinse waters.

Advantages and Limitations. Some advantages of ion exchange for treatment of plating effluents are as follows:

(1) Ion exchange is an economically attractive method for the removal of small amounts of metallic impurities from rinse waters and/or the concentration for recovery of expensive plating chemicals.

(2) Ion exchange permits the recirculation of a high-quality water for reuse in the rinsing operations, thus saving on water consumption.

(3) Ion exchange concentrates plating bath chemicals for easier handling or treatment or subsequent recovery or disposal operations.

Some limitations or disadvantages of ion exchange for treatment of plating effluents follow:

(1) The limited capacity of ion-exchange systems means that relatively large installations are necessary to provide the exchange capability needed between regeneration cycles.

(2) Ion-exchange systems require periodic regeneration with expenditures for regenerant chemicals. Unless regeneration is carried out systematically, leakage of undesirable components through the resin bed may occur. In addition, the usual treatment methods must be employed to dispose of the regenerated materials.

(3) Cyanide generally tends to deteriorate the resins, so that processing of cyanide effluents (except for very dilute solutions) does not appear practical at the present time.

(4) Resins slowly deteriorate with use and the products of deterioration can contaminate the water.

Process Principles and Equipment. Ion exchange involves a reversible interchange of ions between a solid phase and a liquid phase. There is no permanent or substantial change in the structure of the solid resin particles. The capacity of an ion-exchange material is equal to the number of fixed ionic sites that can enter into an ion-exchange reaction, and is usually expressed as milliequivalents per gram of substance. Ion-exchange resins can perform several different operations in the processing of wastewater, including:

(1) Transformation of ionic species

(2) Removal of ions

(3) Concentration of ions.

The performance of some of these functions is illustrated in Figure 7, which is a generalized schematic presentation of the application of ion exchange to treatment of electroplating effluents.(37,38) In practice, the solutions to be treated by ion exchange are generally filtered to remove solids such as precipitated metals, soaps, etc., which could mechanically clog the resin bed. Oils, organic wetting agents, brighteners, etc., which might foul the resins, are removed by passage through carbon filters.

During processing, the granular ion-exchange resin in the column exchanges one of its ions for one of those in the rinse water or other solution being treated. This process continues until the solution being treated exhausts the resin. When this happens, solution flow is transferred to another column with fresh resin. Meanwhile, the exhausted resin is regenerated by another chemical which replaces the ions given up in the ion-exchange operation, thus converting the resin back to its original composition. With a four-column installation consisting of two parallel dual-bed units, as shown in Figure 7, the ion-exchange process can be applied continuously by utilizing the regenerated units while the exhausted units are being regenerated.

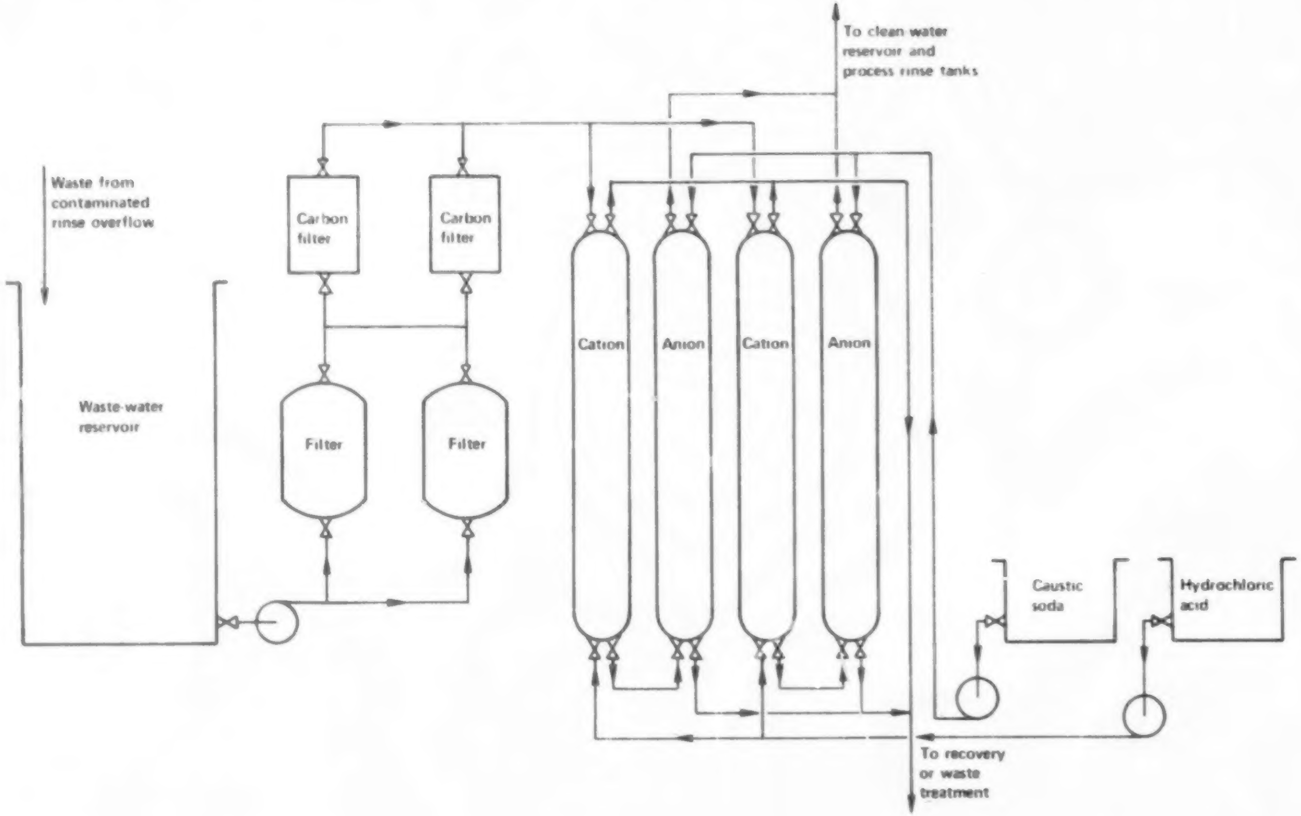

Waste from
contaminated
rinse overflow
Waste-water
reservoir
Carbon
filter
Carbon
filter
Filter
Filter
Cation
Anion
Cation
Anion
To clean water
reservoir and
process rinse tanks
Caustic
soda
Hydrochloric
acid
To recovery
or waste
treatment

FIGURE 7. SCHEMATIC PRESENTATION OF ION-EXCHANGE APPLICATION FOR PLATING-EFFLUENT TREATMENT (7,25)

Practical Operating Systems. Figure 8 shows a schematic drawing of the ion-exchange system used in Plant 11-7 to handle a flow ranging from 2,100 to 4,000 gph of chromium rinse water containing 30 to 250 ppm of hexavalent chromium. The unit saves at least 150,000 liters/d (40,000 gpd) and provides a source of deionized water throughout the plant for preparing plating solutions where good quality water is required. The pure water recycled to the chromium rinse tanks is useful for avoiding spotting of chromium-plated parts. Regenerated solution from the anion-exchange unit is treated by reducing the chromium to Cr^{+3} and precipitating it. Regenerated solution from the cation-exchange unit is combined with the acid-alkali stream for treatment.

Cation-exchange resins are used widely throughout the industry for removing nickel, trivalent chromium, and other impurities from chromium plating baths. Cyanide may be absorbed on ion-exchange resins, but there is danger of leakage of cyanide through the system. An improved three bed system consists of strongly acidic, weakly basic, and strongly basic layers (39). In this system the weak base resin provides a high capacity for cyanide adsorption and the strong base resin provides a back up to take care of cyanide leakage.

Demonstration Status. An ion-exchange system utilizing a short 30 minute cycle, including a 3 to 4 minute back wash, to recover chromic from rinse water has been in operation over a year (40). The resin undergoes very little deterioration since the chromic acid is not deeply absorbed into the resin during such a short cycle.

Ion Exchange for Mixed Effluent. An installation for handling 6,300 gph of wastewater containing nickel, chromates, chlorides and sulfates was installed for recovering 96 percent of the water (32). The cost saving in water was more than three times the cost of operation.

Water Conservation by Evaporative Recovery

Applicability. When rinse water from one type of bath is distilled in an evaporative unit, the concentrate may be returned to the plating bath and the distillate to the corresponding rinse tank, which is useful for closing the loop on a single plating operation. The economics of distillation, from the standpoint of either investment or operating costs imposes a constraint on the size range of distillation equipment. Units with a capacity of the order of 300 gph are used in practice. Such a low rate of flow of rinse water is achieved in many plating operations only by the use of at least three countercurrent rinses, which by itself reduces the wastewater. Evaporative recovery units for all of the rinse cycles would reduce the effluent to zero. So far, recovery units have been installed on rinse tanks following

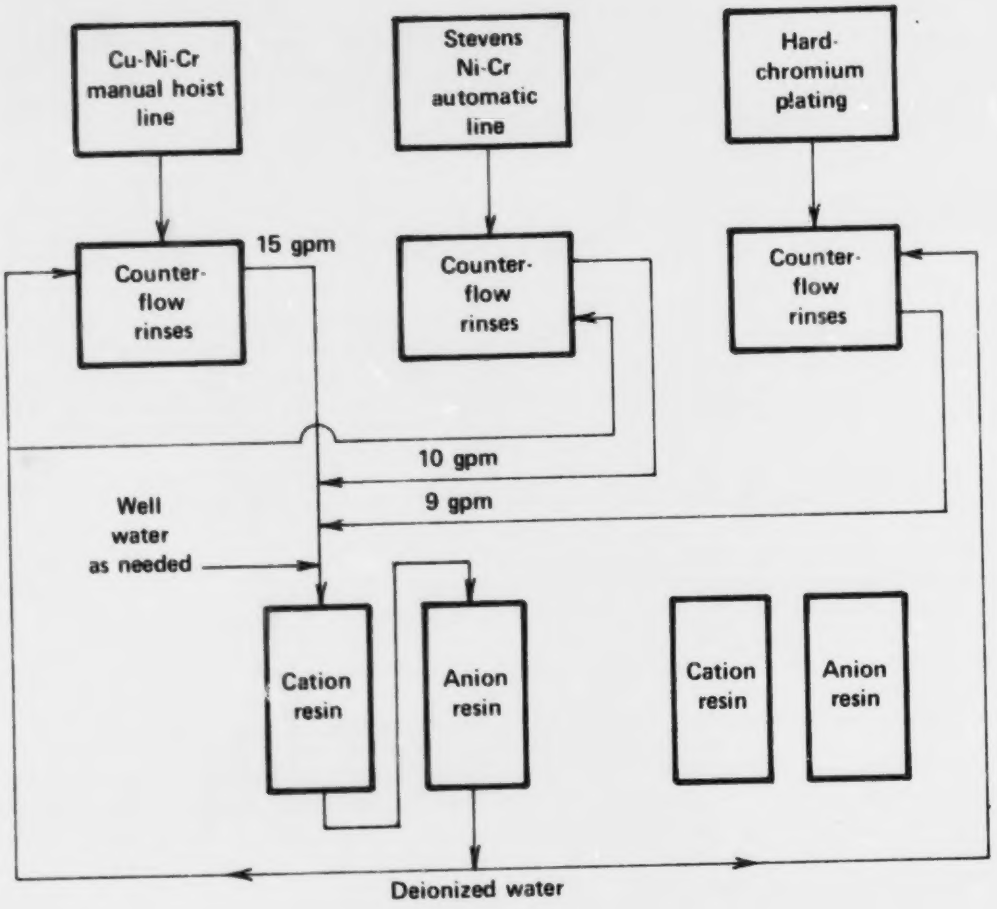

Cu-Ni-Cr manual hoist line
Stevens Ni-Cr automatic line
Hard-chromium plating
Counter-flow rinses
Counter-flow rinses
Counter-flow rinses
15 gpm
10 gpm
9 gpm
Well water as needed
Cation resin
Anion resin
Cation resin
Anion resin
Deionized water

FIGURE 8 . SCHEMATIC PRESENTATION OF ION-EXCHANGE OPERATION AT PLANT 11-8 plating baths in order to recover plating chemicals and return them to the bath and thereby reduce plating costs. The units have not been installed on cleaner or acid dip lines because the cost of chemicals is not sufficient to make recovery worthwhile.

Evaporation is a firmly established industrial procedure for recovering plating chemicals and water from plating waste effluents. Commercial units for handling zinc, copper, nickel, chromium, and other metal plating baths have been operating successfully and economically for periods of one to 10 years or longer. Packaged units for in-plant treatment of plating wastes are available from many manufacturers.

Advantages and Limitations. The following are some of the advantages of using evaporation for handling of plating waste effluents:

(1) Recovers expensive plating chemicals, which were either lost by discharge to a sewer or stream or which had to be treated or destroyed prior to disposal; chemicals concentrated to plating strength can be returned to the plating tank.

(2) Recovers distilled water for reuse in the rinse operations, thus lowering water and sewage costs.

(3) Eliminates or greatly minimizes the amount of sludge formed during chemical treatment and eliminates or reduces the amount requiring disposal by hauling or lagooning.

(4) The use of vacuum allows evaporation to occur at relatively low temperatures (e.g., 110°F) so that destruction of cyanides or other heatsensitive materials is lessened.

(5) The technology of evaporators (conventional and vapor recompression units) is firmly established, so their capabilities are well known and their performances should be readily predictable and adaptable to plating effluent handling.

Some of the limitations or disadvantages of evaporative recovery systems are given below:

(1) The rinse water saving [e.g., 1100 l/hr (300 gph)] is rather small, and by itself does not significantly reduce the rinse water load on the chemical treatment plant.

(2) Evaporative units have relatively high capital and operating costs, especially for the vacuum units. Steam and coolant water are required.

(3) The evaporative units are fairly complex and require highly trained personnel to operate and maintain them.

(4) Separate units are required for handling the waste effluent from each line, as various solutions, such as zinc, nickel, copper, chromium, cannot be mixed for chemical recovery.

The advantages offered by evaporative recovery outweigh the disadvantages when existing chemical treatment facilities are not available. Evaporative recovery is a promising and economical method currently available for handling plating waste effluents and limiting treatment plant size. Where existing chemical treatment (cyanide destruction, chromate reduction, and chemical precipitation) facilities are operating at less than capacity, the economics and practicality of installing new evaporative equipment must be closely evaluated. The small decrease in the rinse water effluent e.g., 1100 l/hr (300 gph) by itself does not warrant the installation of an evaporative system. The savings produced by the recovery of plating chemicals plays the significant role in judging the overall merits of the evaporative system for a specific operation.

Process Principles and Equipment. A representative closed loop system for recovery of chemicals and water from a plating line with a single-effect evaporator is shown in Figure 9. A single-effect evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the plating bath, and distilled water is returned to the final rinse tank. With the closedloop system, no external rinse water is added except for make-up of atmospheric evaporation losses. The system is designed for recovering 100 percent of the chemicals, normally lost in dragout, for reuse in the plating process.

Single-, double-, and multiple-effect evaporators, and vapor-recompression evaporator units are used for handling plating effluent. Open-loop and combined evaporation (i.e., evaporation combined with ion-exchange, reverse-osmosis, or other systems) are also employed for handling plating effluent.

A single-effect evaporator is preferred, if relatively unsophisticated operating personnel are involved, or low initial capital outlay is desired. It's the simplest in design and therefore the easiest to operate. However, it is less economical than a double effect or vapor-recompression unit with regard to utility costs (41). A double-effect evaporator should be considered when lower operating cost is desired with a modest increase in capital investment.

A vapor-recompression evaporator should be considered if no steam or cooling water is available. Where utilities for a conventional steam evaporator are available, the high initial cost of the vapor recompression unit is not economically justified. Its operating cost is the lowest of the three systems. Its dependence on an expensive and complex mechanical compressor is the main disadvantage.

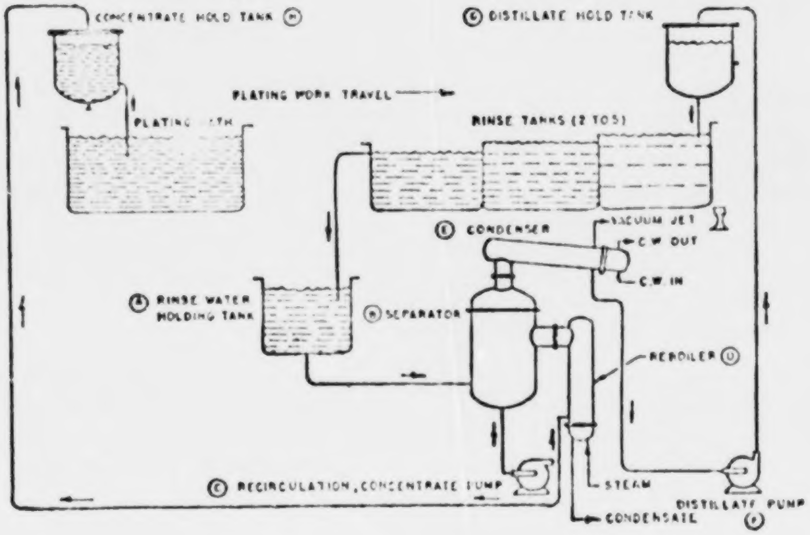

CONCENTRATE HOLD TANK Ⓗ
Ⓖ DISTILLATE HOLD TANK
PLATING WORK TRAVEL
PLATING BATH
RINSE TANKS (2 TO5)
Ⓔ CONDENSER
VACUUM JET
C.W. OUT
C.W. IN
Ⓑ RINSE WATER HOLDING TANK
Ⓐ SEPARATOR
REBOILER Ⓤ
Ⓒ RECIRCULATION, CONCENTRATE PUMP
STEAM
CONDENSATE
DISTILLATE PUMP Ⓕ

FIGURE 9 . REPRESENTATIVE CLOSED-LOOP SYSTEM FOR RECOVERY OF CHEMICALS AND WATER WITH A SINGLE-EFFECT EVAPORATOR

Some sources report considerable maintenance and down time and have dispensed with use of evaporator units. Other sources report little or no trouble and are very satisfied with the operation. It appears that the units can perform very satisfactorily if the installation is properly engineered, and if preventive maintenance and trouble-shooting are carried out by knowledgable personnel.

In some instances, evaporation procedures must be used in combination with chemical or other methods in order to handle small amounts of impurity build-up (e.g., brighteners, carbonates, extraneous metal ions, etc., in closed-loop operation) or for treatment of minor bleed-off streams (open-loop).

Atmospheric evaporation, which uses air flow through packing media in an evaporator, can concentrate plating solution such as chromic acid up to 480 g/l (4 lb/gal)(42). One manufacturer(43) has introduced a new concept for evaporative recovery. A glass shell and tube heat exchanger is mounted vertically and the solution is fed through the bottom. The boiling causes liquid surges that produce a "rising film" effect and an improvement in heat transfer. Vapor and liquid overflow the top of the tubes and are separated in a cyclone. Water with less than 0.05 ppm of chromic acid has been produced from chromium plating rinse water.

Practical Operating Systems. Extensive use is made of evaporators in Plant 20-14, where three units with capacities of 380, 380, and 190 l/hr (100, 100, and 50 gph) are used to completely close the copper cyanide, nickel, and chromium rinse lines respectively. Only the cleaning and acid pickling lines are open and it is roughly estimated that the combined effluent volume from them may be of the order of 11,300 l/hr (3000 gph). The alkali rinse is run directly to the sewer and the acid line is neutralized and run to the sewer without clarification. Small spills and washes are treated chemically. Rearrangement of cleaner and acid dip rinse tanks to counterflow operation could reduce the volume of effluent to a very low level and installation of an evaporator would reduce it further. In contrast to the plating tanks, the cleaners and acids must be discarded periodically so that a completely closed loop on these lines does not seem possible. However, there is no economic incentive to change the present arrangement in this plant to reduce the present effluent volume. One manufacturer has installed over 100 evaporative recovery systems in metal finishing shops.

Figure 10 illustrates an open-loop, partial recovery evaporation system, which is suitable for plating installations where there is an insufficient number (i.e., less than three) rinses. The data shown in Figure 11 are for a cyanide plating line. A small portion of the cyanide dragout that accumulates in the final rinse is not recirculated to the evaporator for concentration. The circulation loop through the evaporator is opened by creating

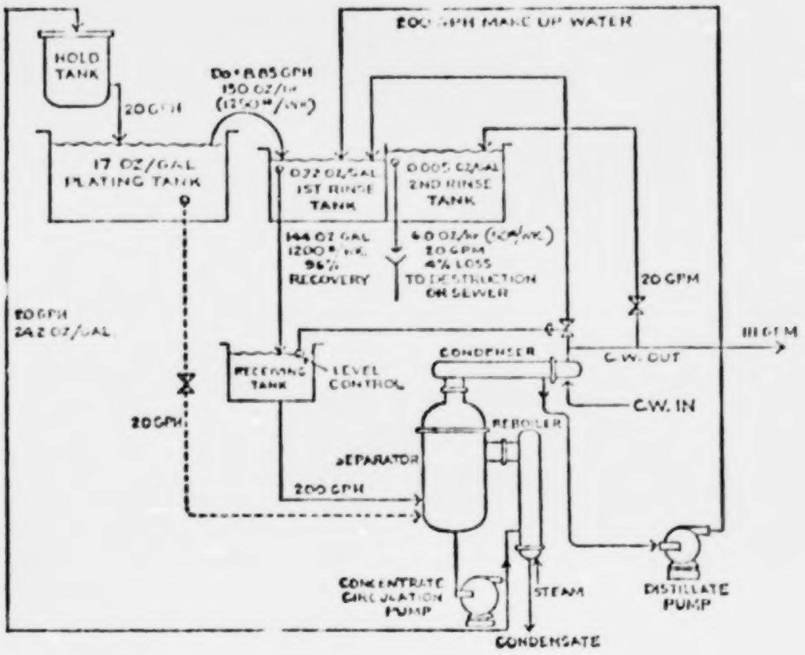

200 GPH MAKE UP WATER
HOLD TANK
20 GPH
D0 + 8.85 GPH
150 OZ/HR
(1250#/WK)
17 OZ/GAL
PLATING TANK
0.72 OZ/GAL
1ST RINSE
TANK
0.005 OZ/GAL
2ND RINSE
TANK
144 OZ GAL
1200#/WK
96%
RECOVERY
6.0 OZ/HR (50#/WK)
20 GPM
4% LOSS
TO DESTRUCTION
OR SEWER
20 GPM
20 GPH
24.2 OZ/GAL
181 GPM
RECEIVING TANK
LEVEL CONTROL
CONDENSER
C.W. OUT
C.W. IN
20 GPH
REBOILER
SEPARATOR
200 GPH
CONCENTRATE
CIRCULATION
PUMP
STEAM
DISTILLATE
PUMP
CONDENSATE

FIGURE 10. REPRESENTATIVE OPEN-LOOP EVAPORATIVE RECOVERY SYSTEM(34)

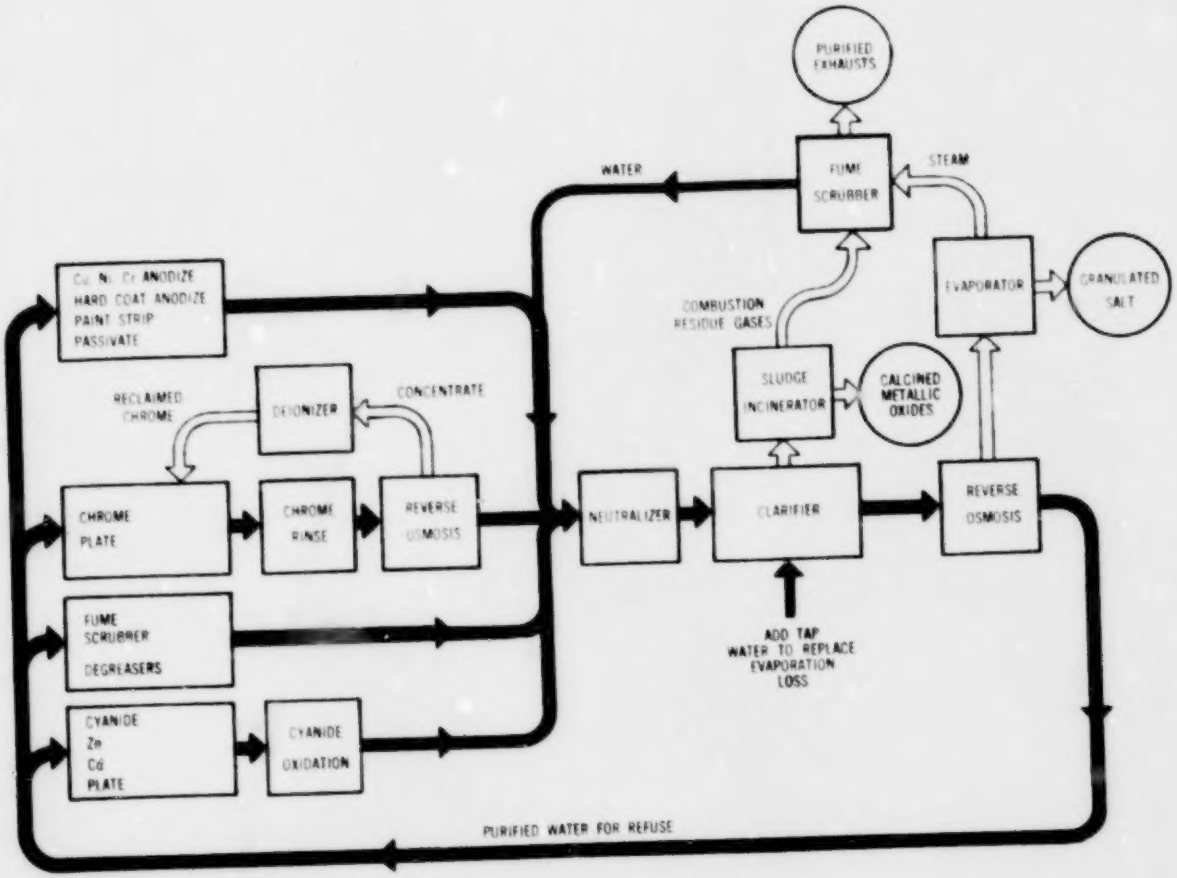

PURIFIED EXHAUSTS
FUME SCRUBBER
STEAM
WATER
EVAPORATOR
GRANULATED SALT
COMBUSTION RESIDUE GASES
SLUDGE INCINERATOR
CALCINED METALLIC OXIDES
Cu Ni Cr ANODIZE
HARD COAT ANODIZE
PAINT STRIP
PASSIVATE
RECLAIMED CHROME
DEIONIZER
CONCENTRATE
CHROME PLATE
CHROME RINSE
REVERSE OSMOSIS
NEUTRALIZER
CLARIFIER
REVERSE OSMOSIS
FUME SCRUBBER DEGREASERS
ADD TAP WATER TO REPLACE EVAPORATION LOSS
CYANIDE Zn Cd PLATE
CYANIDE OXIDATION
PURIFIED WATER FOR REFUSE

FIGURE 11. CLOSED LOOP SYSTEM FOR METAL FINISHING PROCESS WATER AT ROCK ISLAND ARSENAL

another flow path for the cyanide. With only two rinse tanks, the open-loop system can be operated economically, because only about 4 percent of the dragout is lost; this dragout must be treated by some appropriate chemical method before disposal.

Demonstration Status

Atmospheric evaporators have been shown to be practical for recovering chromic acid from spray mists collected in chromium plating venting and scrubbing units. A cation exchanger is used to purify concentrated chromic acid before it is recycled to the plating bath. Several units of the glass "rising film" evaporator are being field tested in applications involving chromic acid solutions.

Water Conservation by Reverse Osmosis

Applicability. Reverse osmosis uses a pressure differential across a membrane to separate a solution into a concentrate and a more dilute solution that may approach the purity of the solvent. It therefore accomplishes the same type of separation as distillation and has been applied in plating installations in the same manner. Small units under 300 gph have been installed to recover plating bath chemicals and make closed-loop operation of a line possible. There are limitations on the acidity and alkalinity of solutions suitable for treatment by reverse osmosis that eliminate some alkaline baths and chromic acid baths from consideration unless modifications are made to the solutions prior to treatment. A recently designed system for Plant 11-22 offers promise that large capacity reverse osmosis systems are possible and therefore not subject to the size constraints of evaporative systems. If so, they should play a key role in the design of plants that will have no liquid effluent.

Most of the development work and commercial utilization of the reverse osmosis process especially for desalination and water treatment and recovery has occurred during the past 10 years. There is a steadily growing number of commercial installations in plants for concentration and recovery of plating chemicals along with recovery of water under essentially closed-loop conditions. Most of the existing commercial installations are for treatment of nickel plating solutions, since reverse osmosis is especially suited for handling nickel solutions and also because of the favorable economics associated with recovery and reuse of expensive nickel chemicals. Commercial reverse osmosis units for handling acid zinc and acid copper processes also have been installed, however. Laboratory and pilot-plant studies directed at handling cyanide and chromium-type effluents are under way.

Reverse osmosis is especially useful for treating rinse water containing costly metals and other plating salts or materials. Generally, the purified water is recycled to the rinse, and the

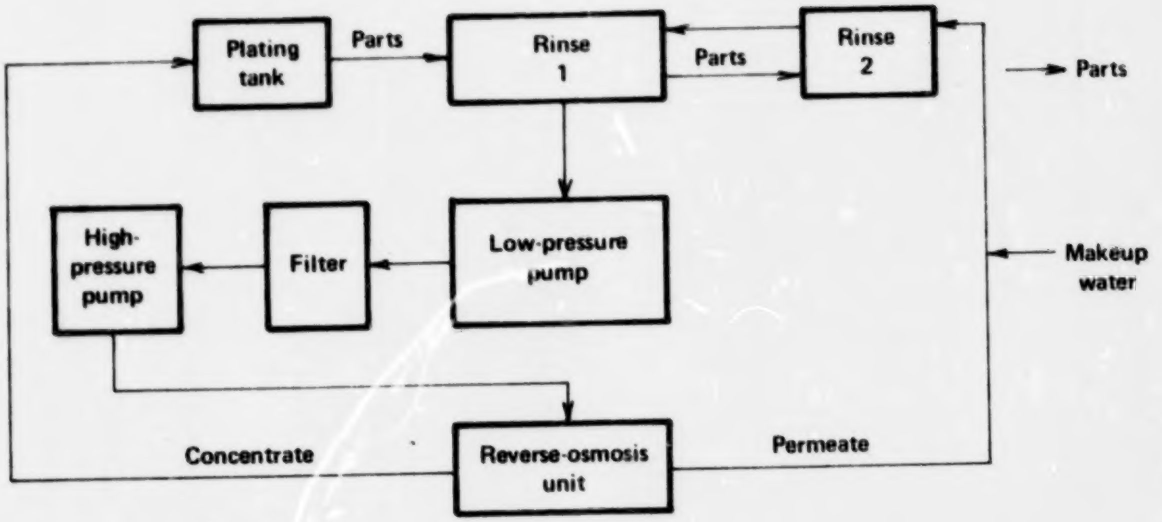

Plating tank
Parts
Rinse 1
Parts
Rinse 2
Parts
Low-pressure pump
Filter
High-pressure pump
Makeup water
Concentrate
Reverse-osmosis unit
Permeate

FIGURE 12. SCHEMATIC DIAGRAM OF THE REVERSE-OSMOSIS PROCESS FOR TREATING PLATING EFFLUENTS

concentrated salts to the plating bath. In instances where the concentrated salts cannot be recycled to the plating tank, considerable savings will be achieved because of the reduced amount of waste-containing water to be treated.

Advantages and Limitations. Some advantages of reverse osmosis for handling plating effluents are as follows:

(1) Ability to concentrate dilute solutions for recovery of plating salts and chemicals

(2) Ability to recover purified water for reuse

(3) Ability to operate under low power requirements (no latent heat of vaporization or fusion is required for effecting separations; the main energy requirement is for a high-pressure pump).

(4) Operation at ambient temperatures 60 to 90° F)

(5) Relative small floor space requirement for compact high-capacity units.

Some limitations or disadvantages of the reversed osmosis process for treatment of plating effluents are listed below:

(1) Limited temperature range for satisfactory operation. (For cellulose acetate systems the preferred limits are 65 to 85° F; higher temperatures will increase the rate of membrane hydrolysis, while lower temperature will result in decreased fluxes but not damage the membrane).

(2) Inability to handle certain solutions (strong oxidizing agents, solvents and other organic compounds can cause dissolution of the membrane).

(3) Poor rejection of some compounds (some compounds such as borates and organics of low molecular weight exhibit poor rejection).

(4) Fouling of membranes by slightly soluble components in solution.

(5) Fouling of membranes by feeds high in suspended solids (such feeds must be amenable to solids separation before treatment by reverse osmosis).

(6) Inability to treat highly concentrated solutions (some concentrated solutions may have initial osmotic pressures which are so high that they either exceed available operating pressures or are uneconomical to treat).

Process Principles and Equipment. Water transport in reverse osmosis (RO) is opposite to the water transport that occurs in normal osmosis, where water flows from a less concontrated solution to a more concentrated solution. In reverse osmosis, the more concentrated solution is put under pressure considerably greater than the osmotic pressure to drive water across the membrane to the dilute stream while leaving behind most of the dissolved salts. Salts in plating baths such as nickel sulfate or copper sulfate can be concentrated to solutions containing up to 15 percent of the salt, by weight (44,45).

Membrane materials for reverse osmosis are fairly limited and the bulk of the development work has been done with specially prepared cellulose acetate membranes, which can operate in a pH range of 3 to 8 and are therefore useful for solutions that are not strongly acid or alkaline, i.e., rinses from Watts nickel baths. More recently, polyamide membranes have been developed that will operate up to a pH of 12, and several of these units are operating in plants for the treatment of cyanide rinse waters.

Figure 11 is a schematic presentation of the reverse osmosis process for treating plating-line effluent. The rinse solution from a countercurrent rinse line is pumped through a filter, where any suspended solids that could damage or foul the membrane are removed. The rinse solution is then raised to the operating pressure by a high pressure pump and introduced into the reverse osmosis unit. The concentrated salt stream is returned to the plating tank, while the dilute permeate stream is returned to the second rinse tank. Currently, several different configurations of membrane support systems are in use in commercial reverse osmosis units. These include plate and frame, tubular, spiral wound, and hollow fine fiber designs.

Practical Operating Systems. Plant 13-2 has installed a reverse osmosis unit on the rinse line of a 6800 liter (1800 gal) bright nickel solution. Solution from a dragout tank immediately following the plating bath is returned directly to the plating bath. Water in the succeeding rinse tanks,containing approximately 25 ppm of nickel, is pumped through a 50-micron prefilter and six reverse osmosis modules at the rate of 450 l/hr (120 gph). Concentrate, at the rate of 23 l/hr (6 gph), is returned to the plating tank and 445 l/hr (118 gph) of water are returned to rinse tanks. The unit is reverse flushed once every two weeks, which produces 23 liters (6 gallons) of waste that is sent to a sludge holding tank. Otherwise the system operates as a closed loop. Life of the modules is estimated to be 2-1/2 years. This system is typical of the systems that have been installed until recently.

A waste-treatment plant designed to produce no liquid effluent has been recently installed at the Rock Island Arsenal (Plant 11-22). Key components in the process are two reverse osmosis units operating in parallel and capable of handling 26,000 l/hr (6800 gph) of effluent. This flow rate is typical for a medium-large plating installation, so that reverse osmosis should be capable of treating total wastewater rather than being used for chemical recovery on individual lines where water volume is much lower. Plant 11-22 had no treatment facilities prior to installation of the new unit. Dilution of plating plant effluent by other effluents at the Arsenal reduced concentrations of pollutants to very low levels. The waste-treatment system could therefore be designed from scratch rather than as an add-on to an existing system. The system that was chosen uses chemical treatment followed by reverse osmosis. The flow diagram in Figure 12 describes Plant 11-22's zero effluent system. The small amount of cyanide is pretreated before being combined with streams from the chromium, acid, alkali, acid copper and nickel baths.

Hexavalent chromium is reduced in the neutralizer tank at pH 8.5. Metal oxides are precipitated at the same time. Effluent from the clarifier goes through a reverse osmosis system. Each of the parallel assemblies contain 26 units that are operated so that 18 units operate in parallel, followed by 6 units in parallel, followed by 2 units in parallel. Thus, these three parallel systems operate in series with each other.

A smaller reverse osmosis unit is used in the plating plant to recover chromium dragout. The acidity of the rinse water is reduced somewhat to prevent deterioration of the reverse osmosis membrane. A deionizer is then used to remove salts formed by the partial neutralization, after which the chromium concentrate can be returned to the plating tank.

Water Conservation by Freezing

Applicability. The freezing process would be capable of recovering metal and water values from plating rinse water to permit essentially closed-loop-type operation if fully developed. The feasibility of using freezing for treatment of plating rinse waters was demonstrated on a laboratory scale using a mixed synthetic solution containing about 100 mg/l each of nickel, cadmium, chromium, and zinc, along with 30,000 mg/l of sodium chloride. Greater than 99.5 percent removal of the metallic ions was achieved in the experiments, with the purified water product containing less than 0.5 mg/l each of the individual plating metals. The separation tests were carried out using the 9500 l/hr (2500-gpd) at a pilot-plant unit.

Process Principles and Equipment. The basic freezing process for concentration and recovery of water from plating effluents is similar to that used for recovery of fresh water from the sea. A schematic diagram of the treatment of plating rinses by the freezing process is shown in Figure 13 (46,47). The contaminated reuse water is pumped through a heat exchanger (where it is

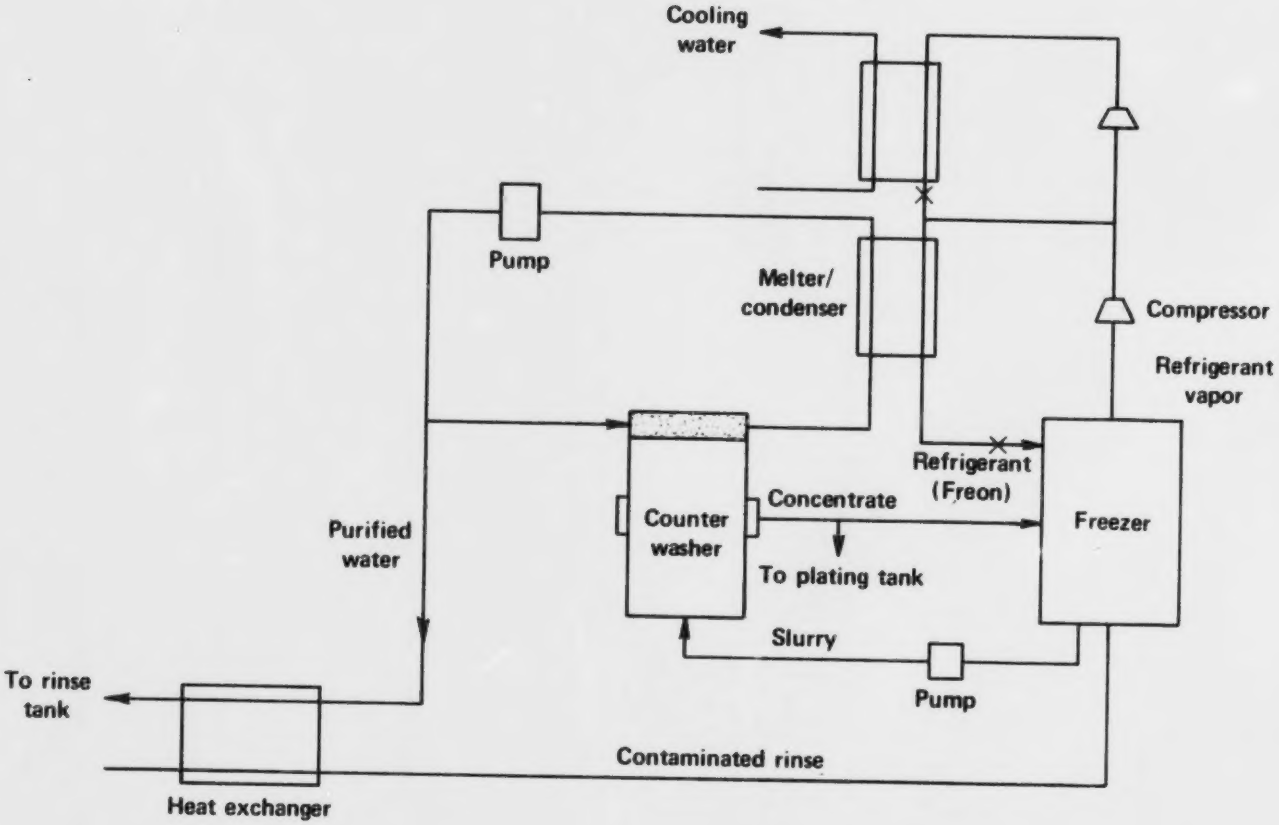

Cooling water
Pump
Melter/ condenser
Compressor
Refrigerant vapor
Refrigerant (Freon)
Concentrate
Purified water
Counter washer
To plating tank
Freezer
Slurry
Pump
To rinse tank
Contaminated rinse
Heat exchanger

FIGURE 13 . SCHEMATIC DIAGRAM OF FREEZING PROCESS FOR RECOVERY OF WATER AND CHEMICALS FROM PLATING RINSES(37,38) cooled by melted product water) and into a freezer. An immiscible refrigerant (e.g., Freon) is mixed with the reuse water. As the refrigerant evaporates, a slurry of ice and concentrated solution is formed. The refrigerant vapor is pumped out of the freezer with a compressor. The slurry is pumped from the freezer to a counterwasher, where the concentrated solution adhering to the ice crystals is washed off. The counterwasher is a vertical vessel with a screened outlet located midway between top and bottom. Upon entering the bottom, the slurry forms a porous plug. The solution flows upward through the plug and leaves the counterwasher through the screen. A small fraction of the purified product water (less than 5 percent) flows countercurrently to the ice plug to wash off concentrated solution adhering to the ice. The ice is pumped to a condenser and melted by the release of heat from the refrigerant vapor which had been originally evaporated to produce the ice, and which had been heated by compression to a saturation temperature higher than the melting point of the ice.

Because of the pump work, compressor work, and incomplete heat exchange, a greater amount of refrigerant is vaporized than can be condensed by the melting ice. Consequently, a heat-removal system is needed to maintain thermal equilibrium. This system consists of a compressor which raises the temperature and pressure of the excess vapor to a point where it will condense on contact with ambient cooling water.

The freezing process offers several advantages over some other techniques. Because concentration takes place by freezing of the water in direct contact with the refrigerant, there is no heat-transfer surface (as in evaporation) or membrane (as in reverse osmosis) to be fouled by the concentrate or other contaminants. Suspended solids do not affect the freezing process and are removed only as required by the end use to be made of the recovered products.

The heat of crystallization is about 1/7 the heat of vaporization, so that considerably less energy is transferred for freezing than for a comparable evaporation operation. Because freezing is a low-temperature process, there will be less of a corrosion problem than with evaporation, and less expensive materials of construction can be employed. The freezing process requires only electrical power, as opposed to the evaporation process which also requires steam generating equipment. The cost of the freezing method may be only 1/3 that for evaporative recovery.

Practical Operating Systems. No commercial utilization of freezing for treatment of waste water from metal finishing is known in the United States. It is understood that practical systems exist in Japan, however.

Demonstration Status. No demonstrations are in progress in metal finishing plants. However, a 9500 liters/day (2500 gpd) unit is in operation to demonstrate desalination of water.

Water Conservation by Electrodialysis

Applicability. Electrodialysis removes both cations and anions from solution and is most effective with multi-valent ions (48). Therefore, it is capable of reducing the concentration of copper, chromium, nickel, and zinc ions from solution whether these metallic ions are complexed or not. Chromate and cyanide ions may also be removed.

Process Principles and Equipment. The simplest electrodialysis system consists of an insoluble anode and an insoluble cathode separated by an anion permeable membrane near the anode and a cation permeable membrane near the cathode. An anode chamber, cathode chamber, and middle chamber are thereby formed. Upon electrolysis anions pass from the middle chamber to the anode compartment and cations pass from the middle chamber to the cathode compartment. The concentration of salt in the central compartment is thereby decreased. By employing several anion and cation permeable membranes between the electrodes several chambers are created. A stream may then be run through several of these chambers in such a pattern that the concentration is reduced in each successive chamber. Another stream is run through chambers in which the concentration is successively increased. The net effect is similar to that of a continuous moving bed ion-exchange column with electrical energy used for regeneration rather than chemicals.

Practical Operating Systems. No practical operating systems have been reported. However, development has resulted in several demonstrations, discussed below.

Demonstration Status. Several demonstrations have shown that electrodialysis is a promising method. Further development and use of the method may be expected. Copper cyanide rinse water may be concentrated sufficiently to be returned to the bath by using two units on a double counterflow rinse system, i.e., between the first and second rinse tank and between the bath and first rinse tank.

Water Conservation by Ion-Flotation Techniques.

Applicability. Ion-flotation techniques have not been developed for application to plating rinse water effluents. If successfully developed into a practical method for plating effluent treatment, ion flotation offers possibilities of reducing the amount of water discharged by 60 to 90 percent for some plating operations. These savings are based on results of small-scale laboratory studies on solutions containing cyanides or hexavalent chromium.

Process Principles and Equipment. Separation of ions from aqueous solutions by a flotation principle is a relatively new concept, first recognized about 25 to 30 years ago. In the ion-flotation operation a surface active ion with charge opposite to that of the ion to be concentrated is added to the solution and bubbles of air or other gas are introduced into the solution to form a froth of the surface-active material. The foam is separated and collapses to form a scum containing an ion-concentrate. Ion flotation combines the technologies of mineral flotation and ion-exchange. A schematic diagram of an ion-flotation cell is shown in Figure 14.

Experimental results indicate that 90 percent of the hexavalent chromium in a 10 to 100 mg/l solution can be removed with primary amine surface active agents (49). However, the amine suffered deterioration when regenerated for re-use, since the removal efficiency dropped to 60 percent after two regenerations of the amine.

Grieves, et al.,(50) have demonstrated the feasibility of using ion flotation on dichromate solutions with a cationic surfactant (ethylhexadecyldimethylammonium bromide). A continuous operation with a retention time of 150 minutes was devised. The feed stream contained 50 mg/l of dichromate. Approximately 10 percent of the feed stream was foamed off to produce a solution containing 450 mg/l of dichromate, while the stripped solution contained 15 mg/l.

Cyanides have been removed from dilute solutions with mixed results. The extraction efficiency from a cadmium cyanide solution containing 10 ppm of cyanide was 57 percent, using primary, tertiary, and quaternary ammonium compounds as collectors. Extraction efficiencies for nickel and iron cyanide solutions were approximately 90 percent.

Practical Operating Systems. There are no practical operating systems.

Demonstration Status. The process has not been demonstrated in an operating plant.

Water Conservation by Electrolytic Stripping

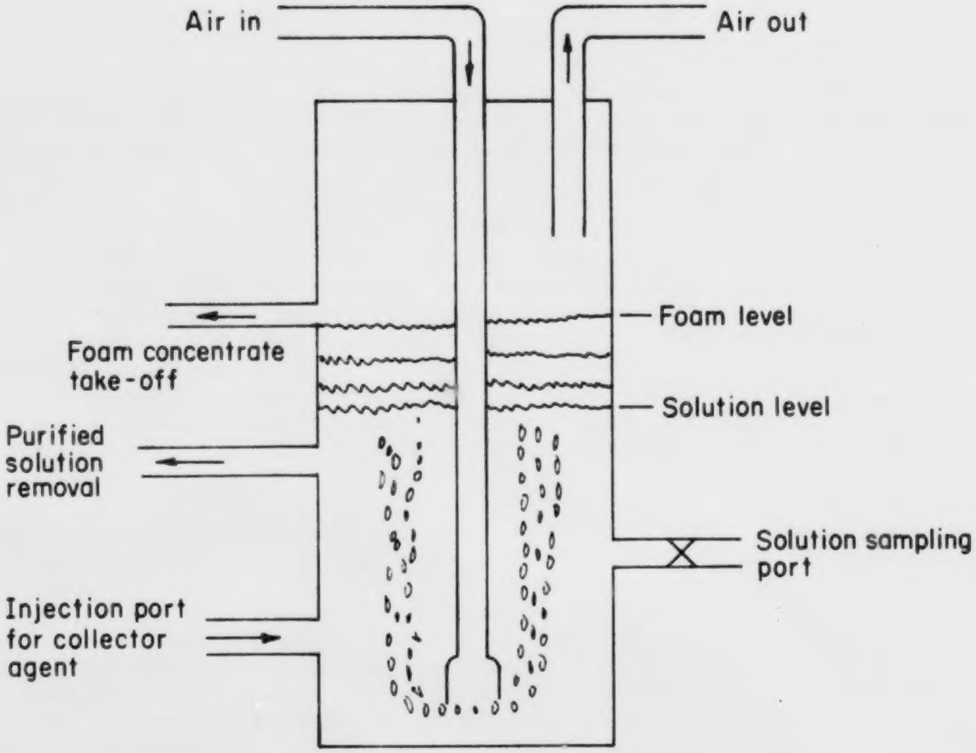

Air in
Air out
Foam level
Foam concentrate take-off
Solution level
Purified solution removal
Solution sampling port
Injection port for collector agent

FIGURE 14. SCHEMATIC DIAGRAM OF ION-FLOTATION CELL FOR TREATMENT OF PLATING EFFLUENT

Applicability. Electrolytic stripping is not in general use for copper, nickel, chromium or zinc, although some procedures have been employed for recovering precious metals. Recent technical developments suggest that they can be used to reduce heavy metal concentrations in the effluent to very low values as well as provide for recovery of the metals.

Process Principles and Equipment. In order to strip a solution by electrodeposition it is necessary that the metallic ions in a dilute solution reach the cathode surface at a sufficient rate so that essentially all of the ions can be deposited in a reasonable time. Surfleet and Crowle(51) have discussed several methods of accomplishing this. One method called the "integrated" system uses baffles in a tank to create a very long path through which the water may be recirculated at a high velocity. The method is suitable only for metals having a relatively high limiting current density for dilute solutions, such as gold, silver, tin. The fluidized bed electrode is a bed of metal spheres or metal-coated glass spheres that is fluidized by pumping the dilute solution through it and causing an expansion of 5 to 10 percent. With spheres of 100 to 300 microns in diameter, a total geometric area of 75 cm^2/cm^3 is obtained. Thus, the current density is very low and the flow of electrolyte through the bed provides the forced convection to support high currents. Another system employs electrodes made of expanded metal and the turbulence around this structure enhances the rate of deposition of metal when solution is pumped past it. Turbulence and an increase in the rate of deposition at a plane electrode may also be promoted by filling the space between electrodes with a woven plastic screen, glass beads, etc.

In another system(52) the electrolyte is introduced into a narrow gap between two porous carbon electrodes. The bulk of the solution (99%) is forced through the cathode where copper is deposited out. Pre-deposited copper on the anodic electrode is dissolved into the one percent of the electrolyte that permeates through this electrode and a copper concentrate is produced. The two electrodes are periodically reversed so that copper deposited from a large volume of solution is dissolved into a small volume of electrolyte. Copper in solution has been reduced from 670 mg/l to 0.55 mg/l in the cathode stream and concentrated to 44 g/l in the anode stream. A similar system has been used for depositing metallic impurities from strong caustic solutions (53).

Practical Operating Systems. There are no practical operating systems in the electroplating industry, although the caustic purification system is in use in the chlor-alkali industry.

Demonstration Status. The porous electrode system(52) is still under development at The University of California and has been scaled up to handle 250 gpd of copper sulfate solution.

Water Conservation by Carbon Adsorption

Applicability. Activated carbon has been used for the adsorption of various materials from solution, including metal ions. Experimental data show that up to 98 percent of chromium can be removed from waste water (49). The treated water can be recycled to the rinse tanks.

Process Principles and Equipment. The process relies upon the adsorption of metal ions on specific types of activated carbon. In the case of Cr^{+6} a partial regeneration of the carbon can be accomplished with caustic solution followed by an acid wash treatment to remove residual caustic and condition the carbon bed for subsequent adsorption cycles. The equipment consists of holding tanks for the raw waste, pumps and piping to circulate the waste through adsorption columns similar to those used for ion-exchange.

Practical Operating Systems. Systems based on adsorption and desorption are still under laboratory development and no practical operating systems are known.

Demonstration Status. Pilot plant equipment has been operated successfully in an electroplating plant treating chromium rinses at a flow rate of 19 liters/min (5 gpm) at concentrations from 100 to 820 mg/l hexavalent chromium. Adsorption was continued until the effluent reached acceptable concentrations of hexavalent chromium.

Water Conservation by Liquid-Liquid Extraction

Applicability. Liquid-liquid extraction has been used on an experimental basis only for the extraction of hexavalent chromium concentrate impurities in a smaller volume, which in turn will have to be treated by other means or suitably disposed of. The fully extracted aqueous phase may be recycled to the rinse tanks. Water savings from 50 to 73 percent appear to be possible.

Process Principles and Equipment. The metal-ion pollutant is reacted with an organic phase in acid solution, which separates readily from the aqueous phase. Metal is subsequently stripped from the organic phase with an alkaline solution. Hexavalent chromium, for example, has been extracted from wastewater at pH 2 with tertiary and secondary amines dissolved in kerosene. After the reaction of the chromium with the amine and phase separation, the chromium is stripped with alkaline solution from the organic phase restoring the amine to its original composition. For liquid-liquid extraction to be feasible the following conditions would have to be met:

(1) The extraction of chromium should be virtually complete.

(2) Reagent recovery by stripping would be efficient.

(3) The stripping operation should produce a greatly concentrated solution.

(4) The treated effluent solution should be essentially free from organic solvents.

(5) Capital and operating costs should be reasonable.

The equipment required consists basically of mechanically agitated mixing and settling tanks, in which the phases are intimately dispersed in one vessel agitation and then permitted to flow by gravity to a settling vessel for separation. Holding tanks for extractant and stripper and circulating pumps for these solutions as well as the purified waste water are necessary. Equipment for liquid-liquid extraction would also include horizontal and vertical columns, pulsed columns and centrifuges.

Practical Operating Systems. Liquid-liquid extraction systems are not known to be operating for treatment of electroplating wastes.

Demonstration Status. Experimental evidence exists indicating that up to 99 percent of chromium can be successfully extracted from rinse waters containing 10 to 1000 mg/l of Cr^{+6}. With 10 mg/l of Cr^{+6} in the rinse water, the treated effluent contained as little as 0.1 mg/l of the ion; with 100 mg/l in rinse water concentration was reduced to 0.4 mg/l. Stripping was effective as long as the amines were not allowed in contact with the chromium for a prolonged period of time which would allow oxidation by Cr^{+6} ions. The effluent, however, contained from 200 to 500 mg/l of kerosene, which is undesirable.

Methods of Achieving No Discharge of Pollutants

Although chemical methods of treating electroplating waste waters are achieving the low effluent discharges suggested in this report, they are not improvable to the point of achieving zero discharge of pollutants. The preceding discussion of water conservation [ion exchange, evaporation, and reverse osmosis (RO)] indicates procedures for achieving no discharge of water. With closed-loop treatment of rinse water in separte streams from each electroplating bath, evaporation or RO can be used to return concentrate directly to the corresponding plating bath.

Impurities in an electroplating bath are increased in concentration when pollutants in rinse waters as recycled and returned to the solution. High concentrations of impurities ultimately affect the quality of the electroplates. Thus, impurity removal becomes necessary. Methods for removing impurities usually contribute pollutants that must be disposed of by chemical treatment. For example, the removal of carbonates from cyanide pollution by precipitation with calcium hydroxide or by freezing involves cyanide and metals, which must be subjected to chemical treatment. Activated carbon for removing organic impurities should be washed before disposal as a solid and the wash water treated to destroy cyanide and/or precipitate metals. Spills that cannot be returned to the segregated recovery cycles must be treated chemically to avoid pollution. These sources of pollutants can be combined with waste water flows from alkaline cleaners, acid dips and other preplating and post plating solutions; from which chemicals cannot be recovered and returned to the process. These preplating and post plating solutions are either changed irreversibly during use or become too contaminated for economic recovery. Replacement or makeup is unavoidable if the solutions are to perform their proper function. Although rinse water can be recycled, a sludge is inevitable in connection with recovering most of the water by chemical treatment. This operation is best performed after mixing the rinse waters from the cleaner and acid dips.

The acid in acid dip solutions gradually becomes neutralized by reaction with the basis metal being processed, and the concentration of the metal increases. Ion exchange can be used in a separate stream of waste rinse water to recycle the water to rinsing. However, the regenerant must be disposed because it contains the dissolved metals that are not recyclable in the acid dipping operation. Most commonly this will be done by chemical precipitation, after mixing with the rinse waters.

A preferred procedure (A) for eliminating discharge of pollutants into navigable streams omits the ion exchange step and concentrates the rinse waters to recycle some of the water and minimize the chemical treatment load as shown in Figure 15. Wash water from spills is fed into either the alkali or acid rinse water holding tank. Obviously dumps of concentrated cleaners and acid dips can be trickled into the respective rinse water holding tank. Rinse water containing post plating pollutants also can be treated by directing it to holding tanks prior to treatment by evaporation or RO and ultimate chemical treatment and precipitation of heavy metal pollutants.

Another procedure (B) for recycling water to rinse tanks and achieving no discharge of pollutants includes chemical treatment of the combined waste from all preplating, plating and post plating operations and separation of solids as discussed on pages 61-79, followed by further treatment of the effluent by evaporation or reverse osmosis to recover high-quality water suitable for rinsing. This water recovery system is used with an RO unit at Rock Island Arsenal (Figure 12). The concentrate from the RO unit (or an evaporator) is evaporated to dryness and disposed of as a granulated salt. When this method for achieving zero discharge of pollutants into navigable streams is adopted with no provision for recovering chemicals reusable in

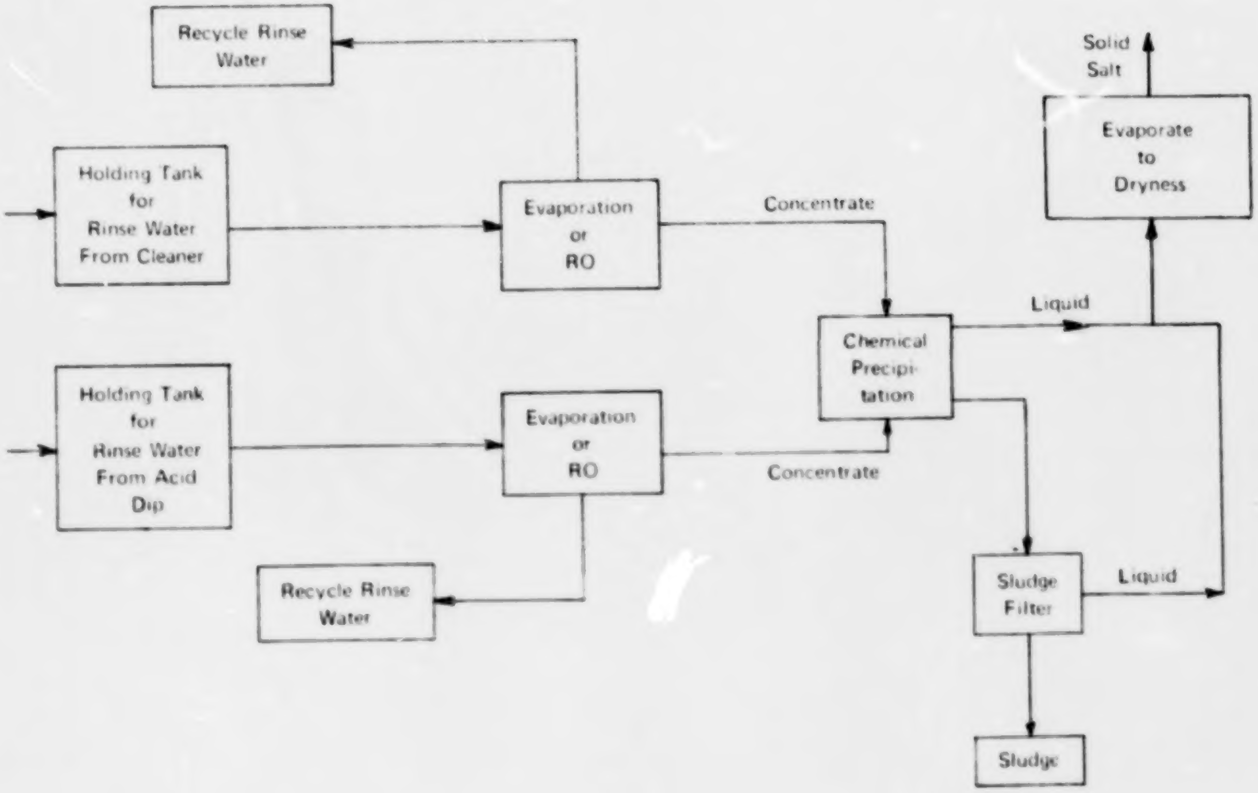

Recycle Rinse Water
Holding Tank for Rinse Water From Cleaner
Evaporation or RO
Concentrate
Solid Salt
Evaporate to Dryness
Liquid
Chemical Precipitation
Holding Tank for Rinse Water From Acid Dip
Evaporation or RO
Concentrate
Sludge Filter
Liquid
Recycle Rinse Water
Sludge

FIGURE 15. FLOW CHART FOR TREATMENT OF WASTE WATER FROM CLEANER AND ACID DIP WHEN PLATING OPERATIONS HAVE SEPARATE STREAM TREATMENT

electroplating baths, costs will be greater than the costs incurred for recycling electroplating chemicals in segregated streams and combining preplating and post plating rinse water for chemical treatment and subsequent evaporation or RO for water recovery.

A possible future development may be direct treatment of the waste water stream by evaporation or reverse osmosis without prior precipitation of the metals. The waste water would need adjustment to a low enough pH to preclude any precipitation which could cause corrosion problems or membrane deterioration. The method would have the obvious merit of reducing the cost of chemical treatment and limiting it to that required for cyanide destruction and chromate reduction. However, the solid residue from evaporation may contain soluble heavy metal salts that would require further treatment before being used as land fill.

SECTION VIII

COST, ENERGY, AND NONWATER QUALITY ASPECTS

Introduction

In this section, costs associated with the degree of effluent reduction that can be achieved by exemplary treatment methods are discussed. Costs also are estimated for evaporation and reverse osmosis technologies that can achieve a further improvement in removing waste water constituents. The nonwater quality aspects concerning disposal of solid waste and the energy impact of the inprocess control and waste treatment technologies also are discussed.

Treatment and Control Costs

Chemical Treatment to Achieve Low Levels of Pollutants

Best Practical Control Technology Currently Available Limitations (Table 1). Costs associated with control technology consistent with the exemplary practice of chemical treatment averaged $10.24/100 sq m (1.52/1000 sq ft) for eight medium-sized and large plants that supplied detailed cost data. The standard deviation for this value was $6.31/100 sq m ($5.86/1000 sq ft) indicating considerable spread from the average value. The operating cost of waste treatment, as a percent of cost of plating was 3.80% with a standard deviation of 2.37%. Plating costs were assumed to be $2.70/sq m (0.25/sq ft) for each deposit applied. (Copper, nickel, chrome on the same part corresponds to three deposits.) The minimum investment cost for a chemical treatment plant is of the order of $50,000 regardless of the size of the plating installation. For plants with a plating capacity of 107 sq m/hr (1000 sq ft/hr), or larger, the investment cost is estimated at approximately $150,000/100 sq m/hr ($140,000/1000 sq ft/hr) of capacity (Figure 16).

The control and treatment technology on which the above costs are based will reduce the discharge of waste water constituents to only 0.1 to 1.0 percent of the amount that would be discharged in the absence of chemical treatment.

The costs of waste treatment in smaller plants was estimated using a model that included chemical treatment consisting of cyanide destruction and hexavalent chromium reduction and precipitation and separation of metals from the combined waste water from preplating, plating, and postplating operations.

A minimum capital investment of $50,000 was assumed for the chemical treatment facility in any small plant. Only 2,000 hours of operation per year (8 hg/day 5 days/week, 50 weeks/yr) was assumed for the small plants in place of 2,625 hours per year for medium-sized Plant 33-1, becuase many small plants confine their operations to only one, 8-hour shift. As a result of these

Preceding page blank

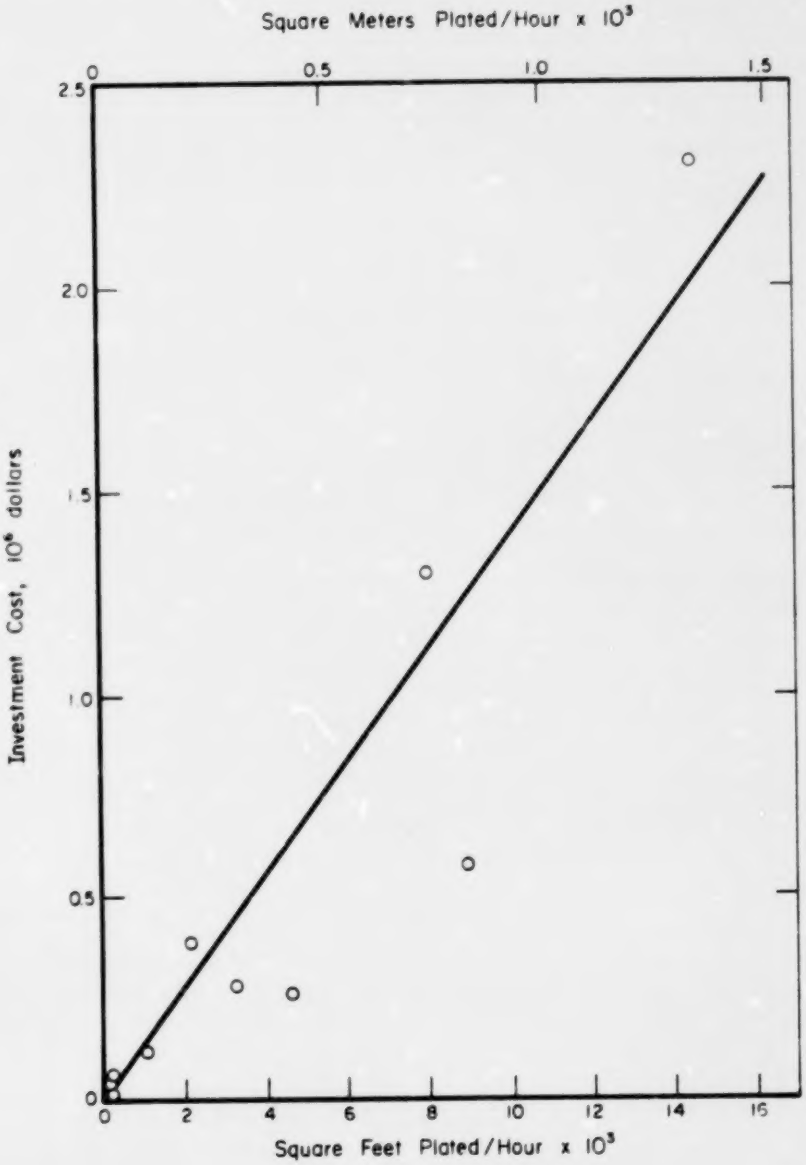


FIGURE 16. EFFECT OF SIZE OF PLATING PLANT ON INVESTMENT COST OF WASTE-TREATMENT FACILITY

assumption, fixed charges and operating costs, based on area planted, are higher for the small plants.

Table 22 shows that estimated costs for meeting the 1977 BPCTCA effluent limitations by chemical treatment are greater for small plants plating less than 33 sq m/hr (360 sq ft/hr) in comparison with the costs for meeting 1977 BPCTCA limitations by larger plants. The figures in Table 22 reflect the fixed costs for capital investment depreciation, interest on the investment and variable costs for chemical treatment. The variable costs for chemical treatment were based on cost data supplied by Plant 33-1. These variable costs at Plant 33-1 were as follows:

Chemicals	$28,439/yr
Sludge disposal	5,144/yr
Labor	23,433/yr
Equipment repair	3,889/yr
Power	3,887/yr
Total	$64,792/yr

Plant 33-1 operates 2,625 hr/yr and has a plating rate of 4,560 sq ft/hr (12,000,000 sq ft/yr). The above cost is about $5.70/100 sq m ($5.30/1000 sq ft), which is about the average cost calculated for 6 other plants. The cost is about $2/1000 gal (assuming 2.5 gal/sq ft) and is typical of values reported for chemical treatment.

According to the estimates in Table 22, the costs for chemical treatment in a small plant with 6 to 10 employees are approximately 7 percent of the total plating costs, assuming that plating costs are $2.70/sq m ($0.25/sq ft). In comparison, costs for chemical treatment in a plant with 2 employees are approximately 18 percent of the plating costs.

As noted previously, the estimates in Table 22 are based on a capital investment of $150,000/100 sq m/hr ($140,000/ 1000 sq ft/hr). Any plant capable of designing and constructing a chemical waste treatment facility at a lower cost will have a lower waste treatment cost per unit area plated. The eight larger plants cited on page 122 obviously were able to reduce their capital investment appreciably because operating costs at these plants averaged only $10.24/100 sq m ($9.52/1000 sq ft), which is only about one half of the estimated cost in Table 22 for small plants with 6 to 20 employees.

New Source Performance Standards (NSPS). New sources that are required to meet the standards of performance recommended in Table 1 have the opportunity of designing and building plants that reduce water flow. Such a reduction can be accomplished by installing counterflow rinsing for each preplating and postplating operation. The capital investment cost for installing a supplemental rinse tank for each operation in a plant plating copper, nickel, chromium and zinc will be approximately $20,000, The impact of this supplemental capital

TABLE 22. ESTIMATED COSTS FOR SMALL ELECTROPLATING FACILITIES WITH NO WASTE TREATMENT TO MEET EFFLUENT LIMITATIONS FOR 1977 AND 1983(a)

Annual Sales $/year(b)	Number of Employees	Treatment Costs(c)					
		Chemical Treatment for BPCTCA (1977)		Chemical Treatment for NSPS		Zero Discharge BATEA (1983)	
		$/100 sq m	$/1000 sq ft	$/100 sq m	$/1000 sq ft	$/100 sq m	$/1000 sq ft
60,000	2	46.1	42.8	62.2	57.8	75.6	70.3
90,000	3	32.6	30.3	43.4	40.3	53.3	49.5
120,000	4	25.8	24.0	33.9	31.5	42.2	39.2
150,000	5	21.8	20.3	28.3	26.3	35.9	33.4
180,000	6	19.3	17.9	24.6	22.9	31.6	29.4
210,000	7	19.3	17.9	24.6	22.9	30.7	28.5
300,000	10	19.3	17.9	24.6	22.9	28.9	26.9
600,000	20	19.3	17.9	24.6	22.9	27.0	25.1

(a) Based on minimum investment of $50,000 for small chemical treatment facility.

(b) Based on manual electroplating operation and $10,000/yr salary per employee and annual sales of $30,000 per employee; 60 sq ft/hr per employee; approximately 330 amperes per employee.

(c) Treatment cost divided by 2.5 is percent of plating costs based on $0.25/sq ft plated.

investment on waste treatment costs for small companies is reflected in Table 22. Estimated costs for a 6 to 20 employee plant plating 33 to 167 sq m/hr (360 to 800 sq ft/hr) amount to approximately 9 percent of the total plating costs, assuming that plating costs are approximately $2.70/sq m ($0.25/sq ft).

Large companies plating more tha 167 sq m/hr (1800 sq ft/hr) will incur costs of no more than $19.30/100 sq m ($17.9/1000 sq ft) to meet new source performance standards. The level of costs for meeting NSPS might be lower if investment costs for chemical treatment are lower than $150,000/100 sq m/hr ($140,000/1000 sq ft/hr).

No Discharge of Pollutants

The elimination of waste water discharge pollutants can be accomplished by water recovery by evaporation-condensation or reverse osmosis in combination with chemical treatment and filtration for acid/alkali waste. Ion exchange is useful for waste water conservation, but is not practical for eliminating waste water constituents in the end-of-process, point source discharge. The preferred mode of operation is to conserve all plating bath chemicals and return them to the plating bath, and concentrate all other chemicals (from preplate and postplate operations) for chemical treatment and disposal in a solid state.

The cost for eliminating waste water pollution using evaporation (and no chemical treatment) in a plant with a plating capacity of 370 sq m/hr ($4000 sq ft/hr) is estimated to range from $5.40 to $17.20/100 sq m ($5.00 to $16.00/1000 sq ft) or 2 to 6.5 percent of the plating costs. The lower figure is associated with the use of a vapor compression system for combined preplating and postplating waste and individual single stage evaporators for recovering plating solution from rinse water following plating operations. The higher figure is associated with single effect units employing steam and cooling water for each preplating, plating, and postplating operation. The capital investment estimates for these evaporation systems are $68,659 and $164,000/100 sq m ($63,810 and $153,000/1000 sq ft) for the vapor compression and single effect evaporation system, respectively.

Costs incurred by a large plant for eliminating waste water pollutants by chemical treatment followed by reverse osmosis are estimated to be of the order of $8.60/100 sq m ($8.00/1000 sq ft) or less, equivalent to about 3 percent of the plating cost. The capital investment estimate for this system is $110,000/100 sq m/hr ($102,100/1000 sq ft/hr). Waste water pollution will be eliminated in this case but there will be a discharge of small amounts of both soluble and insoluble solid wastes.

The incremental cost for achieving zero discharge of pollutants by 1983 by a large facility plating at least 370 sq m/hr (4000 sq ft/hr), which is now equipped for meeting 1977 new source standards or 1977 existing source limitations via chemical treatment is estimated to be $3.39/100 sq m ($3.15/1000 sq ft). This incremental cost assumes that effluent osmosis to recover water and that concentrate from the RO unit will be evaporated to a granulated salt.

Estimated costs for eliminating waste water pollution from small plants that recover no plating solution via evaporation or reverse osmosis are much higher than the costs for achieving zero discharge of pollutants in plants that use evaporation or reverse osmosis to recover plating solution draged into rinse water tanks. The estimates in Table 22 show the higher costs associated with chemical treatment of combined waste water from all preplating, plating, and postplating operations plus reverse osmosis (to recover water) plus evaporation of the concentrate to granulated salt. These estimates vary with the size of the plating facility. Costs increase appreciably as plant size is reduced from 20 to 2 employees. At the 20 employee level, costs for achieving zero discharge of pollutants with no recovery of plating solution amount to approximately 10 percent of the total plating costs (assuming plating costs are approximately $2.70/sq m ($0.25/sq ft)). In comparison a plant with only two employees would entail costs equivalent to about 28 percent of plating costs to achieve the same standard of performance.

The incremental cost for achieving zero discharge of pollutants by 1983 for a small facility plating no more than 167 sq m/hr (1800 sq ft/hr), which is initially equipped for meeting 1977 new source standards via chemical treatment can be estimated from data in Table 22. This increment will vary from $13.40/100 sq m ($12.45/100 sq ft) for a 2 employee plant to $2.40/100 sq m ($2.34/1000 sq ft) for a 20 employee plant.

Cost Effectiveness and Treating Procedures

From an analysis of untreated rinse water and effluent in Plant 33-1 which corresponds to a medium-sized plant (50,000 amperes) with 38 employees, it was possible to calculate the amount of copper, chromium, nickel, zinc, and cyanide removed from the rinse water and determine the amount discharged with the effluent. The volume of discharge for various rinse-tank arrangements and the costs associated with these arrangements were also known. The costs of applying increasingly effective treatment techniques to Plant 33-1 were estimated for the following systems:

(1) A single rinse tank for each rinsing operation; no wastewater treatment

(2) A single rinse tank for each rinsing operation; chemical treatment

(3) Two series rinses for each rinsing operation; chemical treatment

(4) Three counterflow rinses for each rinsing operation; chemical treatment

(5) Single-stage evaporation for each process bath plus 3 counterflow rinses, cleaners and acid dips included, which requires a total of 21 evaporators. All rinse water would be recycled and plating process rinse water would be returned to the plating bath. Thus, no chemical treatment was included

(6) A single-stage evaporator for each process bath and counterflow rinse, except for acid and alkaline preplating and postplating rinses. A large vapor compression unit was assumed for the acid-alkali and postplating stream. Effluent volume reduced to approximately 37.8 lpd (10 gpd). No provision was made for evaporating this very small volume to dryness.

(7) Process lines as they now exist in Plant 33-1. Chemical treatment is used, followed by reverse osmosis on the effluent from the chemical treatment. No provision was made for evaporating the small volume of concentrate from the RO unit.

From these data sources, a cost effectiveness curve was plotted, as shown in Figure 17. The volume of water required for rinsing in single rinse tanks is so large that no precipitation occurs during chemical treatment and the weight of discharged water constituents is not affected by the treatment. The lowest cost on the curve is that now incurred by Plant 33-1 using their present system. The options listed for eliminating discharge of wastewater constituents are associated with costs ranging from $5.40 to $17.20/100 sq m ($5.00 to $16.00/1,000 sq ft).

Nonwater Quality Aspects

Energy Requirements

Chemical Treatment. The electric power used for plating consumes about 0.06 percent of the nation's electrical energy (1.7 x 1012 kilowatt hours). The power required for chemical treatment is approximately 3.2 percent of the power needed for plating, based on data developed from a sample of eight plants with reliable records.

No Discharge of Pollutants. Exclusive use of double effect evaporators for reducing rinse water volume requires steam at a cost that can be one to four times the cost of power for plating, depending upon the degree of rinse water reduction achieved. Use of vapor compression units in part or in whole will reduce the cost of energy requirements to about the same as the cost of electrical energy for electroplating or probably less, and eliminate discharge of pollutants when combined with chemical treatment. Reverse osmosis will achieve the same effluent

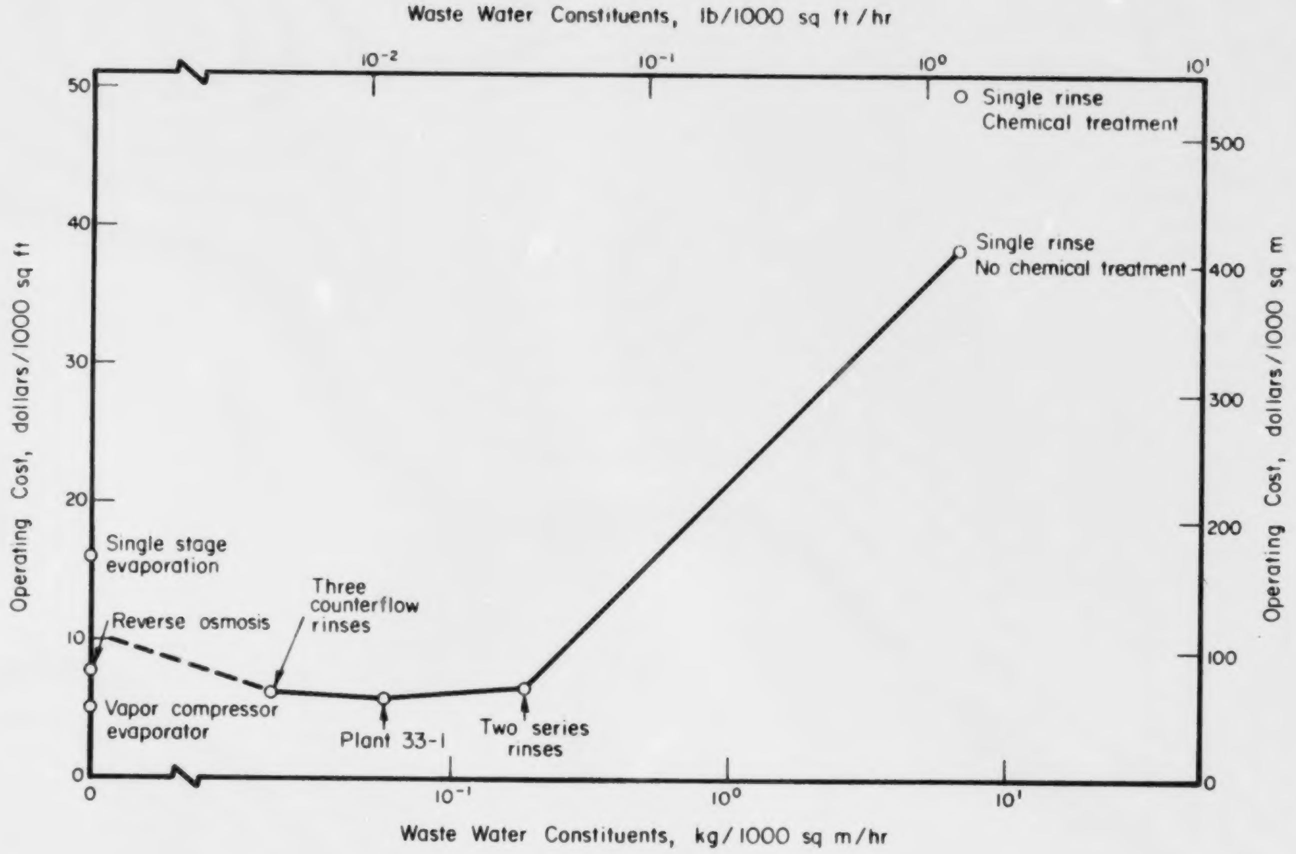


FIGURE 17 . COST EFFECTIVENESS OF TREATMENTS AND IN-PROCESS WATER CONSERVATION TECHNIQUES limitation (when combined with chemical treatment) using 27 percent of the power required for electroplating.

Solids Disposal

The cost of lagooning sludge from a clarifier after chemical treatment has not been considered, because the method is finding less and less favor as a means of disposal. The volume generated by the domestic plating industry is estimated to be about 200,000 cu yd/yr.

For ecological reasons, an alternative to land filling should be sought, such as recovering metal values, if the effluent guidelines and standards of performance recommended in this document are adopted. All solids from the waste treatment should be recycled within the industrial complex.

SECTION IX

BEST PRACTICABLE CONTROL TECHNOLOGY CURRENTLY AVAILABLE, GUIDELINES, AND LIMITATIONS

Introduction

The effluent limitations which must be achieved July 1, 1977, are to specify the degree of effluent reduction attainable through the application of the Best Practicable Control Technology Currently Available. Best Practicable Control Technology Currently Available is generally based upon the average of the best existing performance by plants of various sizes, ages, and unit processes within the industrial category and/or subcategory.

Consideration was also given to:

(a) the total cost of application of technology in relation to the effluent reduction benefits to be achieved from such application;

(b) the size and age of equipment and facilities involved;

(c) the processes employed;

(d) the engineering aspects of the application of various types of control techniques;

(e) process changes;

(f) non-water quality environmental impact (including energy requirements).

The Best Practicable Control Technology Currently Available emphasizes treatment facilities at the end of a manufacturing process but includes the control technologies within the process itself when the latter are considered to be normal practice within an industry.

A further consideration is the degree of economic and engineering reliability which must be established for the technology to be "currently available." Demonstration projects, pilot plants and general use, must show that there exists a high degree of confidence in the engineering and economic practicability of the technology at the time of commencement of construction or installation of the control facilities.

Industry Category and Subcategory Covered

The pertinent industry category is the electroplating industry which is part of the metal finishing industry. This category includes plants using electroplating processes as defined by SIC 3471 (1972) and includes all electroplating processes and their associated pretreatment and post-treatment operations if used in

Preceding page blank

an electroplating process. All other processes and operations defined by SIC 3471 that are not part of processes containing at least one electroplating operation are excluded from this category.

The identification of Best Practicable Control Technology Currently Available and recommended effluent limitations presented in this section cover the subcategory of rack and barrel electroplating of copper, nickel, chromium, and zinc. Effluent limitations are not specified as yet for all metals, all electroplating operations, or all metal finishing processes. However, the control and treatment technology identified is broadly applicable in three other areas: (1) electroplating operations other than rack and barrel; (2) electroplating of metals other than copper, nickel, chromium, and zinc; and (3) other metal finishing processes than electroplating yet to be considered. Recommended effluent limitations applicable to these other subcategories might require a greater or lesser degree of effluent reduction.

Identification of Best Practicable Control Technology Currently Available

Best Practicable Control Technology Currently Available subcategory of rack and barrel electroplating of copper, nickel, chromium, and zinc is the use of chemical methods of treatment of wastewater at the end of the process combined with the best practical in-process control technology to conserve rinse water and reduce the amount of treated wastewater discharged.

Chemical treatment methods are exemplified by destruction of cyanide by oxidation, reduction of hexavalent chromium to the trivalent form, neutralization and coprecipitation of metals as hydroxides or hydrated oxides with settling and clarification to remove suspended solids prior to discharge. The above technology has been widely practiced by many plants for over 25 years. However, the above technology cannot achieve zero discharge of metals because of finite solubility of the metals. In addition, it is not practicable to achieve 100 percent clarification and some small amount of metal is contained in the suspended solids. By optimum choice of pH and efficient clarification, the heavy metal pollutional load may be less than 1 mg of total metal (soluble plus insoluble) discharged for each kilogram of metal electroplated on a basis materials. This degree of pollution reduction can be achieved if the concentrations of all metals is high in the raw waste.

Because of the variety of electroplating processes and metals possible to a single plant and the high cost of in-plant segregation of all waste streams according to metal, coprecipitation of metals is the general practice. There is a different optimum pH of the separate precipitation of each metal as a hydroxide. The pH chosen for the co-precipitation of these metals must be a compromise and will not effect as great a removal as segregated precipitation.

There are several advanced plating bath recovery methods available for closing up the rinse water cycle on individual plating operations. Among these methods are evaporation, ion exchange, reverse osmosis, and countercurrent rinsing. Application of these techniques to pretreatment and posttreatment operations is not known. The corresponding rinse waters plus concentrated solution dumps and floor spills may contain one or all of the pertinent metals in amounts sufficient to require chemical treatment. Thus, chemical treatment of at least the typical acid/alkali stream from pretreatment and posttreatment operations represents the best practicable control technology currently available to achieve the effluent limitations recommended.

Having identified the technology for end-of-process treatment and recognizing the technical and practical limitations on removal of metals by this technology (metal solubility and clarification efficiency), further reduction in the quantity of metal pollutants discharged must be achieved by reduction in the volume of treated water discharged. There are many in-process controls designed to reduce the volume of wastewater which principally results from rinsing. Controls such as reclaim tanks and still rinses designed to to minimize and reclaim dragout of concentrated plating solution can be considered normal practice within the industry. Evaporation losses are made up with the reclaimed solution. Dragout reclaimed does not contribute to the raw waste load normally discharged from remaining rinses. Practicing dragout reclaim is economically wise because it reduces the cost for make up and treatment chemicals. Reduction of dragout leads to reduction in water requirements for rinsing.

Further reduction in rinse water use can be achieved by multiple tank countercurrent rinsing. Unless the rinse water can be used to make up evaporation losses of the bath, there is little reduction in treatment chemical cost and no economic incentive to add more rinse tanks purely for water conservation. However, the use of advanced recovery techniques (evaporation, ion exchange, and reverse osmosis) which concentrate the rinse water sufficiently to allow reclaim of the valuable plating solution provides the economic incentive to use this technology and justifies the cost of recovery equipment plus the cost of installing multitank countercurrent rinsing. However, it should be recognized that the major water reduction occurs because of the installation and use of multitank countercurrent rinsing. The additional reduction in volume of wastewater by recovery of all the rinse water following a plating operation in lieu of chemical treatment usually has limited impact on the total water use in the plant. This is because the volume of rinse waters from pretreatment and posttreatment operations (e.g., the acid/alkali wastewater stream) is often several times larger than the volume of rinses from plating operations.

In the past there has been little economic incentive to reduce water use for rinsing after pretreatment and posttreatment operations. For one reason, the chemicals used in these solutions are not expensive compared to plating solution chemicals and thus they are not purified for reuse. These concentrated solutions are dumped at frequent intervals and there is usually little concern for reducing dragout since the dragout reduces the rate of buildup of impurities and extends the life of the concentrated solution so that less frequent dumping is required. Thus, for pretreatment and posttreatment solutions that are dumped frequently (e.g., once a week), dragout does not influence the quantity of material in the wastewater requiring treatment. However, dragout from these solutions does influence the amount of water required for adequate rinsing.

While sufficient economic incentive is presently lacking to achieve reduction in the volume of the rinse water from pre- and posttreatment operations, there is an opportunity for significant reduction in pollution. The above factors are taken into account in recommending the effluent limitations. Even in plants currently achieving good waste-treatment results, there are further opportunities for reduction in volume of effluent discharged provided there is an economic incentive related to achieving pollution reduction.

Rationale for Selecting the Best Practicable Control Technology Currently Available

General Approach

In determining what constitutes the Best Practicable Control Technology Currently Available, it was necessary to establish the waste management techniques that can be considered normal practice within the electroplating industry. Then, waste-management techniques based on advanced technology currently available for in-process control and end-of-process treatment were evaluated to determine what further reduction in pollution might be achieved considering all the important factors that would influence the determination of best practicable and currently available technology.

Waste Management Techniques Considered Normal Practice in the Electroplating Industry

For that portion of the electroplating industry that discharges to navigable waters it is estimated that a large proportion are currently using chemical treatment for end-of-process pollution reduction. Some of these waste-treatment facilities have been in operation for over 25 years with a continual upgrading of performance to achieve greater pollution abatement. Because of the potentially toxic nature of the chemicals used in the electroplating industry, there is a relatively high degree of sophistication in its water pollution abatement practices. For example, the accidental release of concentrated solutions without treatment to navigable waters is believed to be a rare occurrence today. This is because adequate safety features are incorporated in the design of end-of-process waste treatment facilities in conjunction with good housekeeping within the electroplating facility. This example and other waste management techniques were considered as examples of normal practice within the electroplating industry in determining the Best Practicable Control Technology Currently Available. Other examples of normal practice include:

(1) Manufacturing process controls to minimize dragout from concentrated plating solutions

    (a) proper racking of parts for eary drainage
    (b) slow withdrawal of parts from the solution
    (c) adequate drip time or dwell time over the plating tank
    (d) use of drip collection devices.

(2) Effective use of water to reduce the volume of effluents

    (a) use of rinse water for makeup of evaporation losses from plating solutions
    (b) use of cooling water for noncritical rinses after cleaning
    (c) use of treated wastewater for preparing solutions of waste-treatment chemicals.

(3) Recovery and/or reuse of wastewater constituents

    (a) use of reclaim tanks after plating operations to recover concentrated solutions for return to the plating tank to make up evaporation losses
    (b) reduction in wastewater volume by the use of at least two series flow rinse tanks after each plating operation with return of as much rinse water as possible to the plating tank.

Other waste-management techniques currently in use in one or more plants were evaluated on the basis of reduction in the quantity of pollution in the effluent discharged.

Degree of Pollution Reduction Based on Existing Performance by Plants of Various, Various Control and Treatment Technology

Identification of Best Waste Treatment Facilities

There are about 20,000 facilities for electroplating and metal finishing in the United States and identification of the best plants within the short period of this study required a rational screening approach as follows. The initial effort was directed toward identifying those companies which satisfied two criteria:

1. are engaged in rack and barrel plating of copper, nickel, chromium and/or zinc

2. are achieving good waste treatment.

The 309 companies were identified based on referrals by cognizant people associated with the industry (EPA regional representatives, state pollution control authorities, trade associations, equipment suppliers) and review of permit applications were distributed geographically as shown in Table 23. About 90 percent of the companies were in the three principal regions expected to have high concentrations of electroplating industry: 38 percent in the Northeast (principally EPA Regions I, II and III; 28 percent in the Midwest (EPA Region V): 25 percent in the Southeast (Region IV)).

Of these leads, the 129 companies initially contacted by telephone were primarily in the principal electroplating regions (40 percent in the Northeast; 28 percent in the Midwest; 22 percent in the Southeast). The telephone contacts were made to verify the existence of adequate waste treatment facilities and the type of plating operations pertinent to Phase I. Sufficient information was obtained to characterize the facility and if pertinent to the scope of coverage desired operational data were obtained.

These telephone contacts were continued until 53 plants were identified that provided broad coverage of the industry pertinent to Phase I. Because of the need to achieve variety in electroplating and waste treatment operations, for this study no claim is made that the 53-plant sample provides a true cross-section of the electroplating industry. However, since the sample selection procedure emphasized good waste treatment practice, the sample illustrates that good waste treatment can be achieved by a variety of plants, job and captive, large and small, few and many different plating processes, in various geographic locations discharging to municipal systems or directly to navigable waters.

As shown in Table 24 the 53 plants consisted of 39 captive facilities and 14 job shops; 28 of these plants discharged treated effluent directly to streams and the other 25 discharged to municipal systems. The relative size of the plants in terms of plating capability and raw waste load to be treated is best indicated by the installed amperes for plating. Most electroplaters readily knew their installed rectifier capacity in amperes which represented their potential production capability. A lesser number readily knew their production capacity in area plated per unit time or production rate of parts processed through the facility.

TABLE 23. GEOGRAPHICAL DISTRIBUTION OF GOOD ELECTROPLATING WASTE TREATMENT FACILITIES BASED ON INITIAL REFERRALS, COMPANIES CONTACTED FOR INFORMATION, AND REPRESENTATIVE FACILITIES EVALUATED IN DETAIL

Area	Referral	Contact	Evaluated
EPA Region I			
Connecticut	32	12	3
Massachusetts	26	2	2
New Hampshire	2		
Rhode Island	1		
Maine	2		
Vermont	3	2	1
EPA Region II			
Delaware	3	1	
New Jersey	11	2	2
New York	18	13	4
EPA Region III			
Maryland	7		
Pennsylvania	7	4	2
Virginia	3		
West Virginia	2		
EPA Region IV			
Alabama	16	4	1
Florida	14	7	2
Georgia	5	4	
Kentucky	4	2	1
Mississippi	5	2	
North Carolina	15	1	
South Carolina	11	1	
Tennessee	8	7	2

(Continued)

TABLE 23. GEOGRAPHICAL DISTRIBUTION OF GOOD ELECTROPLATING WASTE TREATMENT FACILITIES BASED ON INITIAL REFERRALS, COMPANIES CONTACTED FOR INFORMATION, AND REPRESENTATIVE FACILITIES EVALUATED IN DETAIL

(Continued)

Area	Referral	Contact	Evaluated
EPA Region V			
Illinois	22	10	3
Indiana	14	6	6
Michigan	18	13	7
Minnesota	4	1	1
Ohio	21	19	11
Wisconsin	8	2	
EPA Region VI			
Arkansas	4	4	3
EPA Region VII			
Iowa	10	2	1
Kansas	1	1	
Missouri	6	4	1
Nebraska	1	1	1
EPA Region VIII			
Utah	1		
EPA Region IX			
California	3	1	
EPA Region X			
Washington	1	1	

TABLE 23. GEOGRAPHICAL DISTRIBUTION OF GOOD ELECTROPLATING WASTE TREATMENT FACILITIES BASED ON INITIAL REFERRALS, COMPANIES CONTACTED FOR INFORMATION, AND REPRESENTATIVE FACILITIES EVALUATED IN DETAIL

(Continued)

Area	Referral	Contact	Evaluated
EPA Region V			
Illinois	22	10	3
Indiana	14	6	6
Michigan	18	13	7
Minnesota	4	1	1
Ohio	21	19	11
Wisconsin	8	2	
EPA Region VI			
Arkansas	4	4	3
EPA Region VII			
Iowa	10	2	1
Kansas	1	1	
Missouri	6	4	1
Nebraska	1	1	1
EPA Region VIII			
Utah	1		
EPA Region IX			
California	3	1	
EPA Region X			
Washington	1	1	

TABLE 24. CLASSIFICATION BY SIZE, TYPE OF FACILITY, AND EFFLUENT DISCHARGE FOR 53 ELECTROPLATING FACILITIES SELECTED FOR EVALUATION

Relative Size	Amperes Installed	Captive		Job	
		Municipal	Stream	Municipal	Stream
Very large	over 200,000	--	1	--	1
Large	50,000-200,000	7	2	1	2
Medium	10,000-50,000	4	11	5	3
Small	1,000-10,000	7	6	1	1
Very small	less than 1,000	--	1	--	--

Classification of 53-Plant Sample

Table 25 shows the scope of coverage for the 53 plants in terms of the mix of possible plating operations and variety of control and treatment technologies. Most plants (32) are equipped for decorative plating of copper-nickel-chromium and of these about half (14) also plate zinc. About 75 percent of the plants in the sample that plate zinc also use a subsequent chromate conversion. The remaining 21 plants provide most of the expected process combinations of copper, nickel, chromium and/or zinc plating that might be found in the industry. The 53 plants in the industry sample include the variety of control and treatment combinations to be found. Most plants (38) used some type of chemical treatment such as continuous (C), batch (B), and/or integrated (I) to treat the metals and cyanide associated with the plating operation. A few plants use electrolytic treatment (L) and one uses reclaim tanks for recovery (R). The other 15 plants included examples of a variety of advanced in-process controls combination of evaporation (E), ion exchange (D) and reverse osmosis (O). Most of the plants used end-of-pipe chemical treatment (continuous or batch) for at least the acid/alkali wastewater stream.

The classification of the 53 plants by size (based on amperes), number of employees in plating for all shifts and waste-treatment method is shown in Table 26. Figure 18 shows that more than half of these plants had fewer than 20 employees per shift.

Of the 53 plants, 26 were visited for on-site inspection and verification of information. The data on rated or installed current capacity are shown in Table 27. Figure 19 shows the same data for total installed current capacity and indicates that 50 percent of the plants had less than 18,000 amperes. The normal use of installed current capacity was 67 percent based on the 23-plant average of the fraction of total rated capacity used shown in Table 27. Thus, it was estimated that 50 percent of the plants used less than 12,000 amperes.

Figure 20 shows the relation of installed rectifier capacity to number of employees per shift in electroplating for the 53-plant sample. The average value calculated is about 1000 amperes installed/ employee. Based on an estimated typical 65 percent use of installed capacity, the average value would be 650 amperes used/employee per shift. The large amperage per employee for automatic plating machines (over 5000 amperes/employee) would be expected to result in considerable spread in the data. Thus, number of employees is not a definitive indicator of plant size in terms of pollutional potential. Amperes as related area plated is a more definitive measure of plant size and raw waste load.

Waste Treatment Results

Table 28 shows the treated effluent data and plant effluent discharge rate (average hourly rate in 1/hr). Figure 21 shows

TABLE 25. CLASSIFICATION OF 53 FACILITIES EVALUATED BY MIX OF PLATING OPERATIONS AND TYPE OF WASTE TREATMENT AND IN-PROCESS CONTROLS

Waste Treatment (a) and Control	Metals Electroplated															
	Cu	Ni	Cr	Zn	Cu Ni	Cu Cr	Cu Zn	Ni Cr	Ni Zn	Cr Zn	Cu Ni Cr	Cu Ni Zn	Ni Cr Zn	Cu Ni Zn	Cu Ni Cr Zn	Totals
C							2			1	6	1			6	16
B		1	1	1	1			1			1	1				7
CB											3					3
CBR															1	1
LC															2	2
I			1					1			2				1	5
IC															2	2
IB								1								1
IR											1					1
EI				2									1			3
EC												1				1
EB				1	1											2
EDC															1	1
EDB											1					1
E				2											1	3
D											2					2
OB											1					1
OIC											1					1
Totals	0	1	2	6	2	0	2	3	0	1	18	3	1	0	14	

(a) See Footnote (e) Table 25 for definition of symbols.

TABLE 26. SOURCE OF INFORMATION AND CLASSIFICATION BY SIZE AND WASTE-TREATMENT METHOD

Company Code No.[(a)]	Reference[(b)]	Data Obtained[(c)]	Size of Facility: Employees in Plating	Size of Facility: Relative Size[(d)]	Classification[(e)]
1-16	S	T	10	M	C/S/CCC-CC
3-1	13	P	19	M	C/S/--BEE-
3-3	13, L	P	31	M	C/S/-IEI-B
3-4	11	P	40	M	C/S/EB--BB
6-3	S, 12	P	6	S	C/S/BII--B
6-12	S, 13	P	54	M	C/M/ENCEEN
6-29	32	T	20	S	J/S/CCICIC
8-4	S	T	12	S	C/M/CCC-CC
8-5	S	T	50	S	C/L/CCC-CC
11-8	S, 13, L	P	165	L	J/S/CCDECC
11-13	S	T	18	M	J/S/CCC-CC
11-22	33, L	P	--	L	C/M/OOO-BC
12-3	15	P	90	M	J/M/NEENNC
12-5	S	T	25	M	J/M/CCCCAC
12-6	S	T	120	VL	J/S/DDE-BB
12-8	S	P	100	L	C/M/CCCCCC
12-9	S	T	25	M	C/S/IRI-IC
12-12	S	T	70	L	C/M/---EE-
13-2	L	T	20	M	C/M/COI-CC
15-1	13	T	6	S	C/M/---EE-
19-2	18	T	70	M	J/S/LCLLLC
19-3	1, 21	P	30	M	J/S/--I--C
20-1	S	P	7	S	C/S/C-CCCC
20-6	S	T	80	L	C/S/CCB-BC
20-7	S	P	25	M	C/S/CCBCBC
20-10	L, 18	T	250	L	C/M/-II--C
20-13	5, 17, L	P	6-10	M	C/S/ICIIIC
20-15	5	T	13	S	C/M/-BB--B
20-17	5	T	50	L	C/S/CCCCCC
21-3	S	T	16	S	C/S/BBBBBB
23-3	7, 11	T	200	L	J/M/CCC-CC
25-1	7, S	T	69	L	C/M/CCCCCC
28-9	S	T	15	M	J/L/-B--BB
28-11	2	T	25	L	C/M/CCCCCC
30-1	14	P	52	M	J/M/LCLLLC
30-5	2	T	30	M	C/S/IIIIIC
30-7	19	T	15	M	C/S/III-IC
30-8	19	P	24	M	C/M/--NBBB
33-1	16, 5, S	P	38	L	J/S/CCCCCC
33-2	S	T	10	S	C/S/BNN-NB
33-3F	13	P	1	S	C/M/--IEEC
33-3U	13	P	5	S	C/M/--IEEC
33-6	17, L	P	100	M	J/M/CCC--C
33-8	5	P	3	VS	C/S/--B--B
33-9	S	P	16	S	J/M/NDD-NC
33-11	S	P	12	M	C/M/C-CCCC
33-15	S	P	20	VL	C/S/CCB-BC
33-20	S	P	12	S	C/M/CCCCCC
33-21	5	T	18	L	C/M/--CCCC
36-1	L	P	25	M	C/S/BBBBBB
36-2	32	P	13	S	C/M/INI-IB
40-4	5	T	40	M	C/S/DDD--C
43-1	S	T	2	S	C/S/RCRBBB

Footnotes appear on the following page.

FOOTNOTES FOR TABLE 26

(a) Company identification by number for this report.

(b) Source of lead to company.

(c) Information from telephone call (T) or first-round visit (P).

(d) Relative size based on total installed rectifier capacity in amperes for plating:

VL = very large, >200,000 amperes
L = large, 50,000 to 200,000 amperes
M = medium, 10,000 to 50,000 amperes
S = small, 1,000 to 10,000 amperes
VS = very small, >1,000 amperes.

(e) Classification by type of facility (1st letter):

J = job shop or independent
C = captive plating facility,

where the treated effluent is discharged,

S = stream (or storm sewer to stream)
M = municipal sanitary treatment system,
L = liquid effluent disposed of on land

and the following coded waste treatment or in-process control used for each constituent of the final effluent considered in the order; copper, nickel, chromium, zinc, cyanide, acid/alkali:

A = adsorption
B = batch chemical treatment
C = continuous chemical treatment
D = ion exchange
E = evaporation
I = integrated
L = electrolytic
N = no treatment beyond pH adjustment
O = reverse osmosis
R = reclaim rinsing techniques.

TABLE 27 SIZE OF PLATING OPERATIONS (RATED AND USED)

Company Code No.	Cu	Ni	Cr	Zn	Total	Fraction of Rated Capacity Used				
						Cu	Ni	Cr	Zn	Total
1-16	1,500	9,000	6,000		16,500	0.8	0.8	1.0		0.9
3-1				10,000	10,000					
3-3		10,000	25,000	5,825	40,825					
3-4	800	12,000			12,800					
6-3		2,500	3,000		5,500					
6-12	5,000	5,000		20,000	35,000[(a)]	0.3	0.8		0.7	0.7
6-29	600	1,500	3,000	1,000	6,100	0.04	0.05	0.2	0.5	0.1
8-4	1,500	200	1,500		3,200					
8-5	1,000	2,300	1,000		8,160[(b)]					
11-8	8,150	25,150	23,150	27,150	94,600[(c)]	0.3	0.6	0.5	0.3	0.5
11-13	3,000	8,000	8,000		19,000					
11-22	500	1,000	72,000		73,500					
12-3	600	17,000	8,000	10,000	35,600		0.4	0.5	1.0	0.6
12-5	4,000	2,000	8,000		14,000					
12-6	80,000	120,000	63,000		263,000	1.0	0.8	0.9		0.9
12-8	6,150	9,250	15,600	32,500	63,500	0.3	0.4	0.3	0.5	0.4
12-9	1,000	16,000	16,000		33,000	1.0	0.5	1.0		0.8
12-12				133,000					0.8	0.8
13-2	6,000	5,000	4,000		15,000	1.0	1.0	1.0		1.0
15-1				6,000	6,000				1.0	
19-2	2,000	11,000	2,000	9,000	24,000	0.8	0.9	1.0	0.8	0.9
19-3*			44,250		44,250			0.7		0.7
20-1	300			3,200	3,700[(d)]					
20-6	13,000	23,000	16,000		57,000					
20-7	5,000	20,000	7,500		32,500					
20-10		45,000	30,000		75,000			0.9	1.0	1.0
20-13	1,400	4,000	3,000	2,500	10,900					
20-15		8,650	250		8,900					
20-17	27,000	43,500	50,000	9,000	129,500	0.5	0.6	0.7	0.3	0.6
21-3	750	600	750		2,100					
23-3	20,000	10,000	10,000	35,000	75,000					
25-1	2,650	3,000	20,000	48,650	74,300					
28-9		6,000			21,700[(e)]					
28-11	35,100	62,000	25,000	12,500	134,600	0.4	0.4	0.5	0.7	0.5
30-1	6,750	8,000	6,000	450	21,200					
30-5	3,300	4,000	1,500	1,200	10,000					
30-7	2,000	10,000	8,000		20,000					
30-8				15,000	15,000				0.8	0.8
33-1	3,000	23,000	8,500	15,250	49,750	0.2	0.2	0.7	0.8	0.5
33-2	400	350			1,250[(f)]					
33-3F				7,000	7,000					
33-3U				7,000	7,000					
33-6	7,000	8,500	10,000		25,500					
33-8*			250		250					
33-9	1,000	4,000	4,500		9,500					
33-11	3,000			12,000	15,000					
33-15	63,000	273,000	118,000		454,000	0.7	0.7	0.8		0.7
33-20	3,000	200		3,000	6,200					
33-21			20,000	32,600	52,600			0.2	0.6	0.6
36-1	4,500	4,500		6,000	16,000[(g)]	0.4	0.4		0.9	0.6
36-2	250	1,500	1,500		3,650[(h)]	1.0	0.3	0.3		0.3
40-4	8,000	8,100	10,000		26,100	0.9	0.9	0.9		0.9
43-1	1,500	3,000	1,500	1,500	7,500		0.1	0.4	0.4	0.2

Footnotes appear on the following page.

FOOTNOTES FOR TABLE 27

(a) Includes an additional 5,000 amperes for Cd.

(b) Includes an additional 1,000 amperes for Cd; 2,825 amperes for Ag; 35 amperes for Au.

(c) Includes an additional 11,000 amperes for Cd.

(d) Includes an additional 100 amperes for Cd and 100 amperes for Sn.

(e) Includes an additional 5,700 amperes for Ag and 10,000 amperes for Sn.

(f) Includes an additional 300 amperes for Cd and 200 amperes for Ag.

(g) Includes an additional 1000 amperes for anodizing.

(h) Includes an additional 400 amperes for Cd.

TABLE 28 TREATED EFFLUENT DATA

Company Code No.	Classification	Treated Effluent, mg/l							Total Flow lph(a)
		TSS	Cu	Ni	Cr^{6+}	Cr_T	Zn	CN	
1-16	C/S/CCC-CC		0.5	1.0	0.0	1.5		0.0	39,700
3-1	C/S/--BEE-					0.05	0.15		34,000
3-3	C/S/-IEI-B		0.018	0.002		0.16			15,400
3-4	C/S/EB--BB		0.08	0.48	0.74				1,100
6-3	C/S/BII--B	3.4	0.08	0.6	0.01	0.14	0.26	<0.1	6,800
6-12	C/M/ENCEEN		0.53	19.6	<0.05	2.75	18.4	1.1	9,100
6-29	J/S/CCICIC			0.6	0.3			0.07	18,900
8-4	C/M/CCC-CC		0.1	0.06	0.05	0.28		<0.01	47,300
8-5	C/L/CCC-CC					<1.0		0.01	94,600*
11-8	J/S/CCDECC		0.03	0.16	0.01	0.02	0.12	0.01	123,000
11-13	J/S/CCC-CC		0.1		<0.01	1.7		0.01	28,000
11-22	C/M/OOO-BC		0.3	0.00	0.1		0.1		401,000
12-3	J/M/NEENNC		<0.5	1.5	1.0	1.5		6.5	55,300
12-5	J/M/CCCCAC		2.4	2.2		4.1	0.4	9.9	28,000*
12-6	J/S/DDE-BB		1.0	1.0	0.05	1.0		0.2	78,700
12-8	C/M/CCCCCC		0.7	0.2		0.6	0.6	0.1	68,000
12-9	C/S/IRI-IC		<1.0	<1.0		0.05	<1.0	0.025	39,700
12-12	C/M/---EE-							1.0	47,300
13-2	C/M/COI-CC		3	2.5			0.28	<1	11,000
15-1	C/M/---EE-						<5	<3	3,800
19-2	J/S/LCLLLC				0.03	0.32		1.0	28,400
19-3	J/S/--I--C		0.15	<0.20	0.40	0.65	0.12		3,100
20-1	C/S/C-CCCC	13	0.18		0.03		1.3	0.06	42,600
20-6	C/S/CCB-BC		0.096	0.39	0.16	0.2		<0.01	44,700
20-7	C/S/CCBCBC	25	<0.1	<0.7	<0.01	0.2	0.25	<0.01	68,000
20-10	C/M/-II--C			2		2			39,400
20-13	C/S/ICIIIC		<0.1	0.3		<0.1	0.2	<0.1	34,000
20-15	C/M/-BB--B			<1.0		<1.0			68,000
20-17	C/S/CCCCCC	21	0.41	0.48	0.05	0.33	0.08	0.0016	250,000
21-3	C/S/BBBBBB		0.2	0.25		0.2	0.03	0.01	12,000
23-3	J/M/CCC-CC		1.75			10.0	2.0	0.2	473,000*
25-1	C/M/CCCCCC		<0.07	0.8		0.15	0.87	<0.03	55,300
28-9	J/L/-B--BB		<10.0					<0.01	2,800*
28-11	C/M/CCCCCC	15	0.41	0.5	0.15	1.2	0.35	0.05	170,000
30-1	J/M/LCLLLC		0.2	7.0	0.01	<5.0	7.9	0.35	30,000
30-5	C/S/IIIIIC		<0.2	<0.2	0.045	0.75	0.45	<0.05	91,000
30-7	C/S/III-IC		<3.5						8,700
30-8	C/M/--NBBB					<1.0	5.0	<0.04	62,500
33-1	J/S/CCCCCC		0.2	0.3	0.06	0.31	0.8	0.13	32,500
33-2	C/S/BNN-NB	9.5	1.47	1.0	<0.015	0.14		0.55	42,600*
33-3F	C/M/--IEEC					0.05	0.05	0.13	11,200
33-3U	C/M/--IEEC					0.05	0.05	0.13	8,100
33-6	J/M/CCC--C	8.5	<0.1	<0.05	<0.5				21,600
33-8	C/S/--B--B					0.05			32,500
33-9	J/M/NDD-NC	9.5	0.13	1.6	0.38	0.52			3,800
33-11	C/M/C-CCCC		3.1		0.6	1.8	0.5	<0.01	11,400
33-15	C/S/CCB-BC	20	0.2	0.42	0.04	0.23	0.09	0.025	295,000
33-20	C/M/CCCCCC		0.21		0.195	0.274	0.5	0.008	11,500
33-21	C/M/--CCCC	106	0.12	0.3	0.04	0.11	0.82	0.05	129,000
36-1	C/S/BBBBBB		<0.01	<0.01		<0.06	0.14	<0.01	36,000
36-2	C/M/INI-IB		0.16	7.5	0.03	0.03	0.13	0.02	8,700
40-4	C/S/DDD--C		<2	<5		1			17,000
43-1	C/S/HCRBBB		0.29	0.35		0.03		0.01	620*

(a) An asterick after the total flow means an assumed 8-hour work day; values could be lower by a factor of 3 if liters per day was based on 24-hour work day.

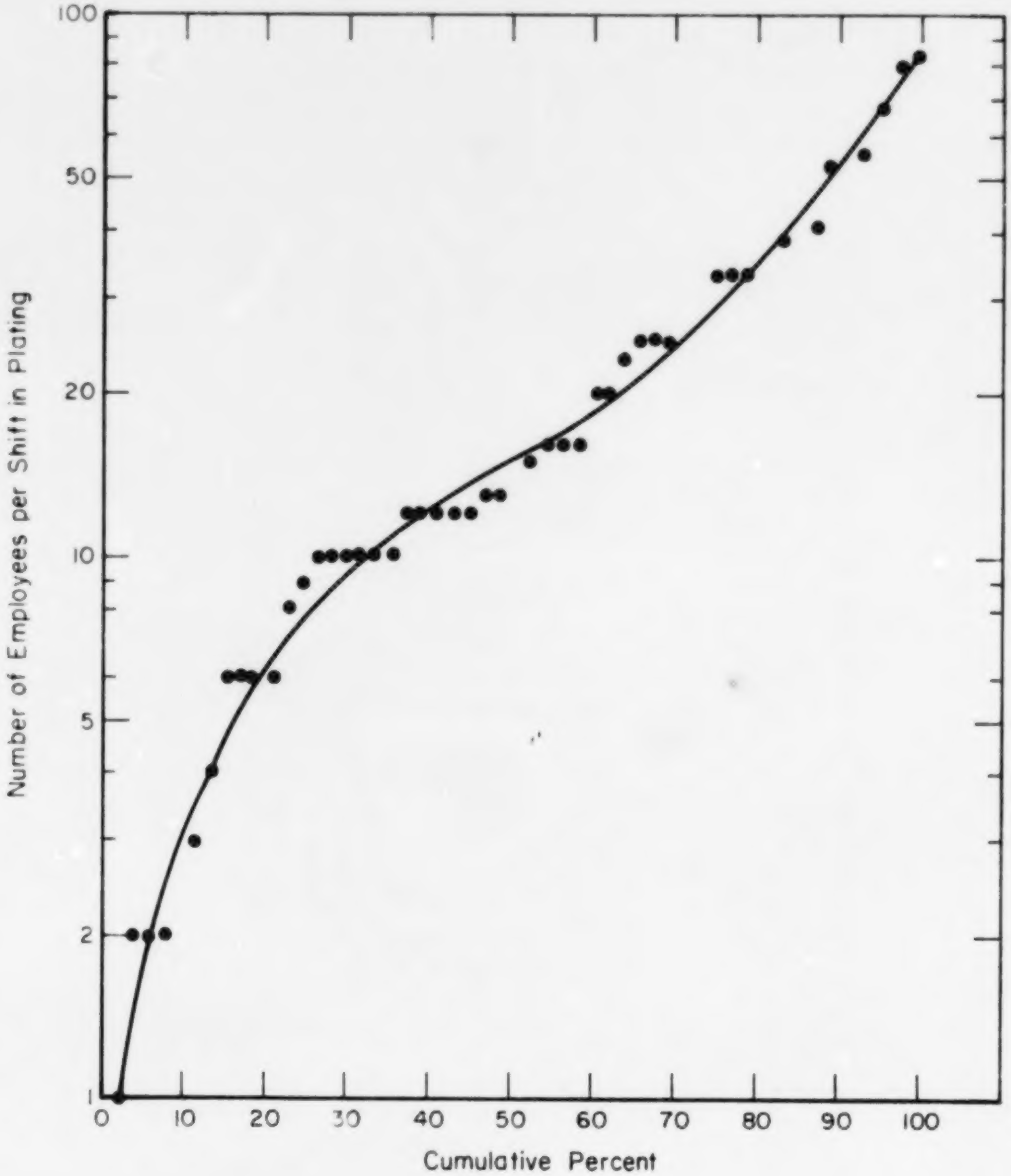


FIGURE 18. EMPLOYEES PER SHIFT IN PLATING VERSUS CUMULATIVE PERCENTAGE OF 53 PLANTS

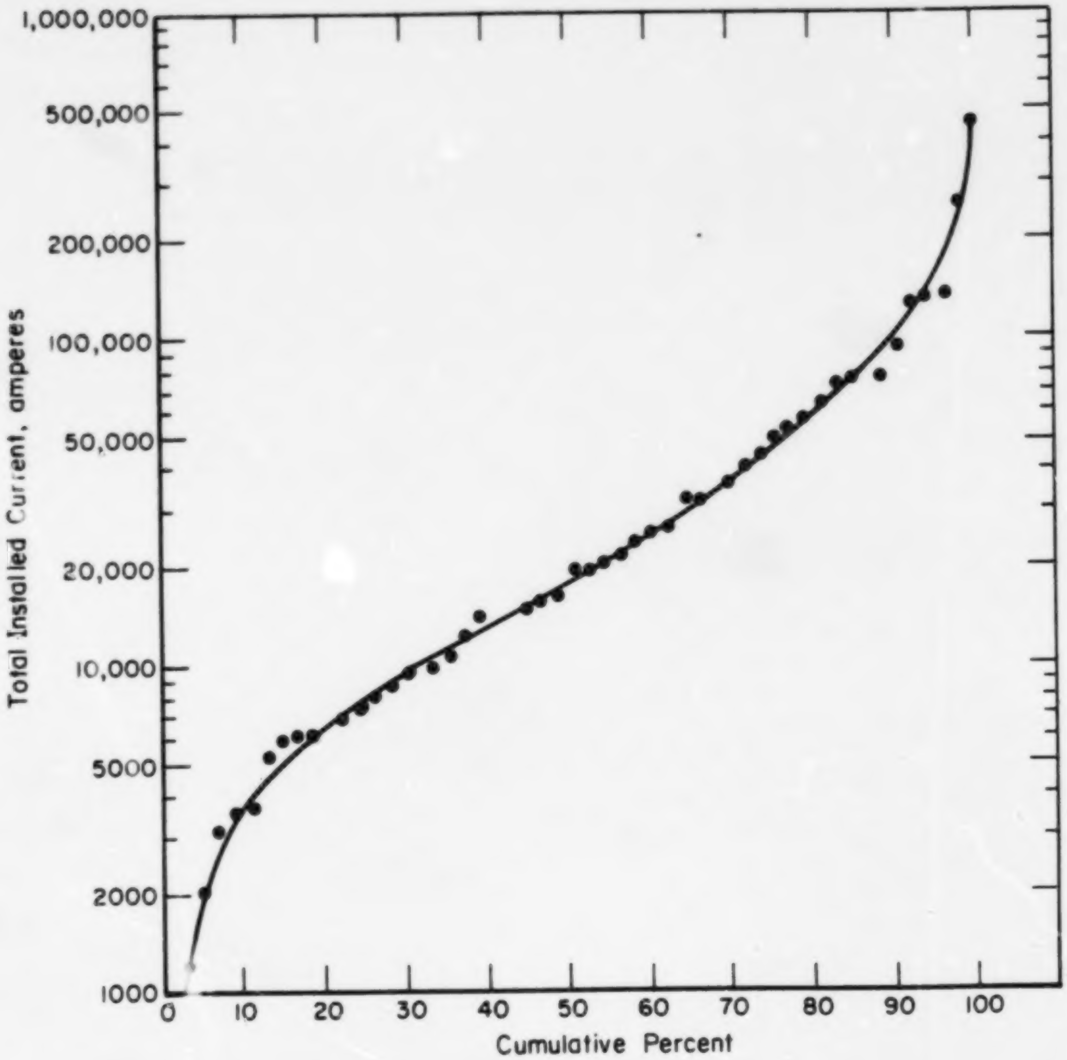


FIGURE 19. TOTAL INSTALLED CURRENT FOR PLATING VERSUS CUMULATIVE PERCENTAGE OF 53 PLANTS

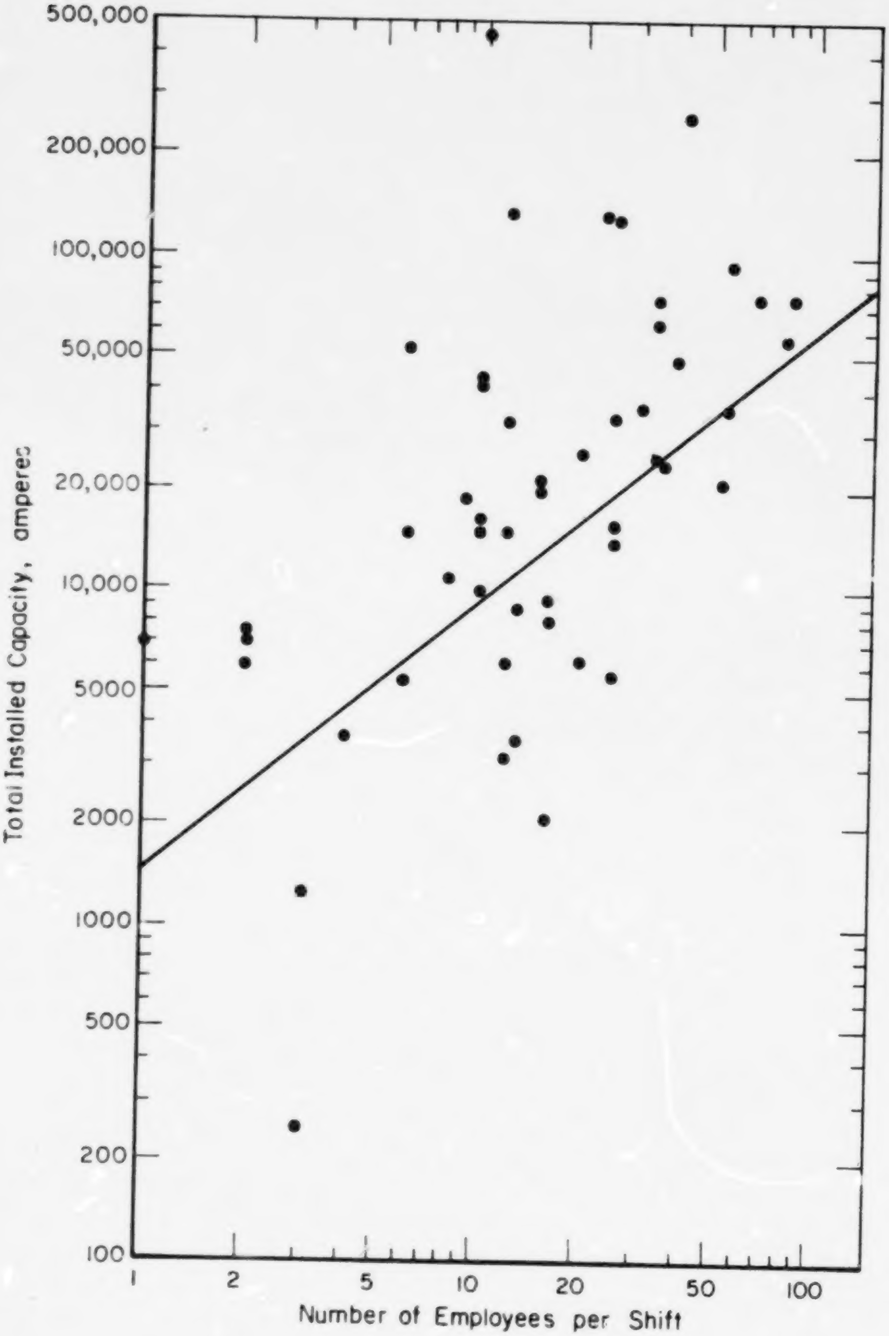


FIGURE 20. INSTALLED RECTIFIER CAPACITY IN AMPERES FOR ELECTROPLATING VERSUS NUMBER OF EMPLOYEES PER SHIFT IN ELECTROPLATING FOR 53 PLANT SAMPLE (RATIO OF AMPERES USED TO AMPERES INSTALLED IS TYPICALLY 65 PERCENT)

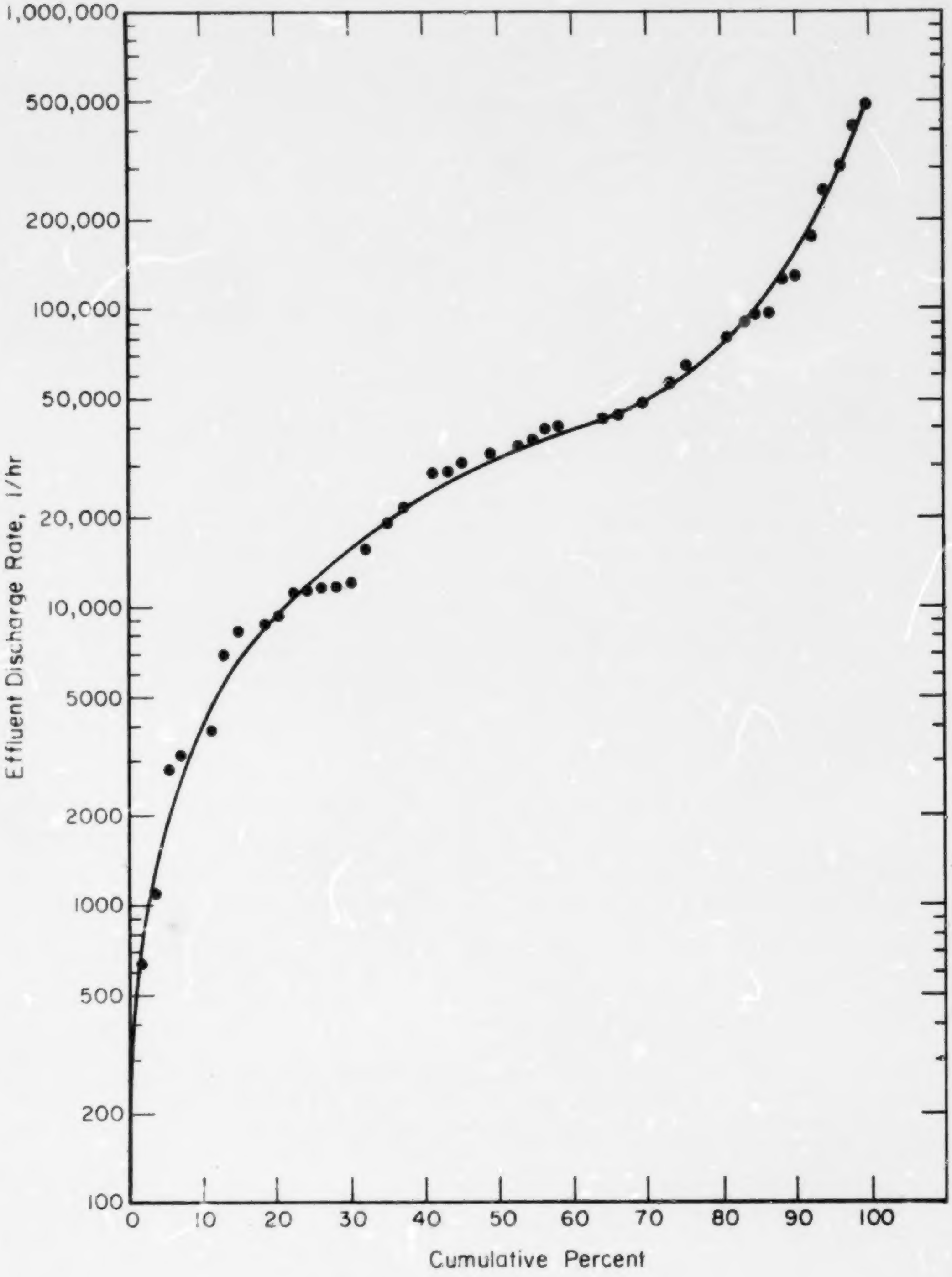


FIGURE 21 . EFFLUENT DISCHARGE RATE VERSUS CUMULATIVE PERCENTAGE OF 53 PLANTS that 50 percent of the 53 plants evaluated have an effluent of less than 34,000 l/hr. Most plants analyze for total metal and oxidizable cyanide (rather than total cyanide). These concentration values reported by the companies are typical average values (monthly period or longer). Figure 22 shows the range of concentration of metals and cyanide (oxidizable) typically achieved by those plants which report that pollution parameter. The results are representative of chemical treatment. Figure 22 shows that 50 percent of the plants have values less than the following:

Cu	0.2 mg/l
Ni	0.5 mg/l
Cr^{6+}	0.055 mg/l
CrT	0.3 mg/l
Zn	0.3 mg/l
CN	0.04 mg/l.

From the limited data on total suspended solids in Table 28 about half of the plants are achieving less than 15 mg/l.

Table 29 provides a comparison of the waste treatment results for all 53 plants on the basis of total installed amperage. The total plant effluent (l/hr) in Table 28 was divided by the total installed current capacity (amperes) in Table 27 to obtain the plant water use (kg/AH which is numerically equivalent to l/AH) shown in Table 29. The water use multiplied by the concentrations (mg/l) of each constituent in the treated effluent shown in Table 28 gave the waste discharged (mg/AH) shown in Table 29. Table 29 provides an approximate intercomparison of the waste treatment results for various plants for several pollutant parameters over a wide range of plant sizes. The data have been normalized by the use of total current. However, in order to draw valid conclusions for direct comparison of two plants in Table 29 additional information is needed on any unusual differences in thickness of deposit (e.g., the two extreme cases of thick chromium plating are noted) or the fraction of the rated current that is normally used (Table 27).

Figure 23 shows that 50 percent of the 53 plants achieving a water use of less than 1.35 l/AH (or kg/AH) based on total installed current. The water used would be about 2.0 l/AH based on the assumption of 67 percent of the rated capacity normally used as indicated previously. Since the latter water use (l/AH) is independent of the concentration values (mg/l) achieved in chemical treatment, it is possible to multiply the median water use and median concentrations to estimate the waste discharge (mg/AH) which should be achievable for most plants:

Cu	0.4 mg/AH
Ni	1.0 mg/AH
Cr^{6+}	0.11 mg/AH
CrT	0.6 mg/AH
Zn	0.6 mg/AH
CN(oxid)	0.08 mg/AH.

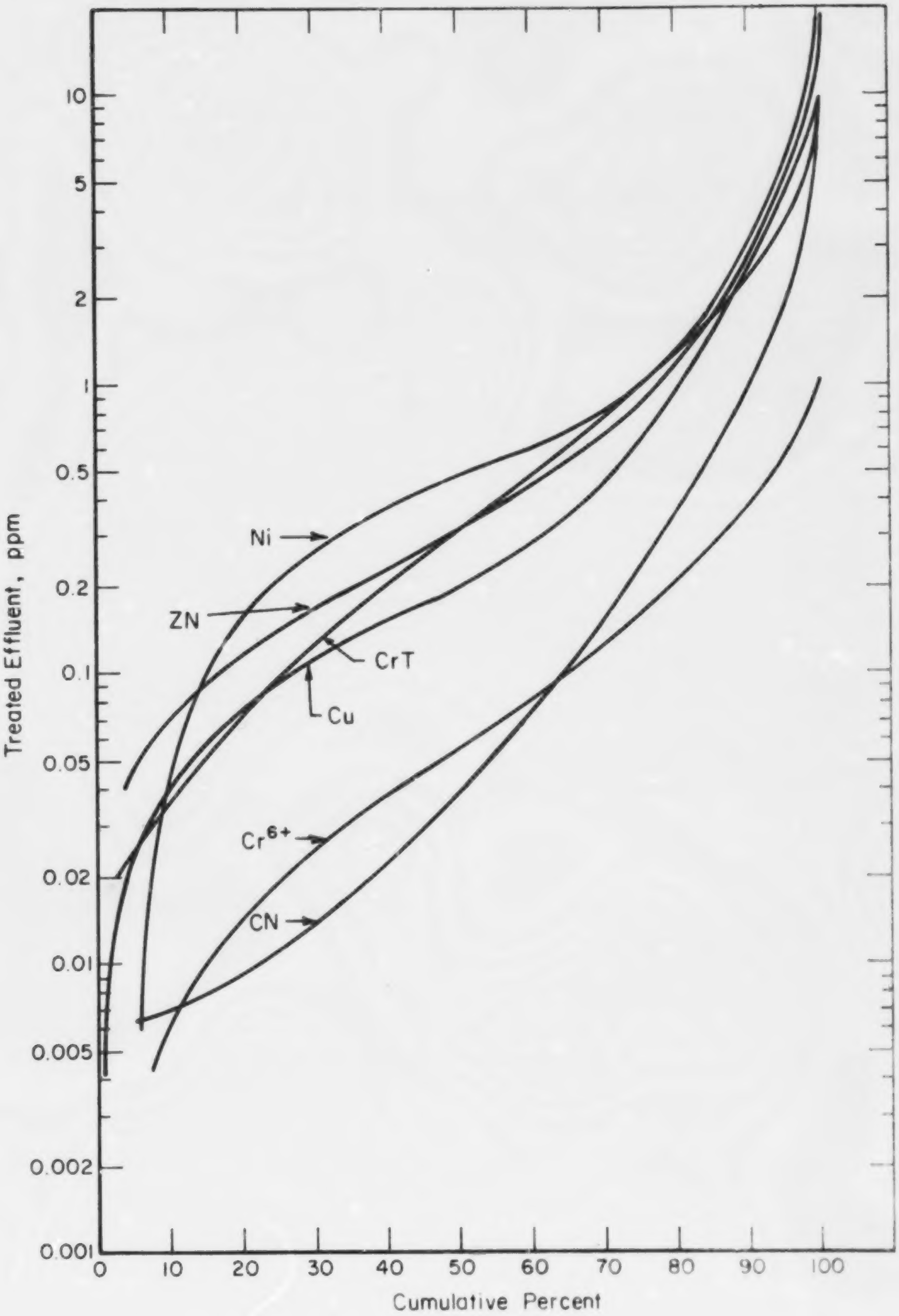


FIGURE 22. COMPOSITE OF POLLUTANT PARAMETERS IN TREATED EFFLUENT VERSUS CUMULATIVE PERCENTAGE OF PLANTS

TABLE 29 COMPARISON OF TREATED EFFLUENT DATA BASED ON TOTAL AMPERAGE

Company Code No.	Classification	Water Use, kg/AH(a)	Waste Discharge, mg per AH						
			TSS	Cu	Ni	Cr^{+6}	CrT	Zn	CN
1-16	C/S/CCC-CC	2.4		1.1	2.4	0.22	3.6		0.22
3-1	C/S/--BEE-	3.4					0.17	0.51	
3-3	C/S/-IEI-B	0.38		0.007	0.0008		0.061		
3-4	C/S/EB--BB	0.09		0.007	0.043	0.022			
6-3	C/S/BII--B	1.2	4.2	0.098	0.74	0.012	0.17	0.32	0.12
6-12	C/M/ENCEEN	0.27		0.14	5.3	0.014	0.74	5.0	0.30
6-29	J/S/CCICIC	3.1			1.9	0.93			0.22
8-4	C/M/CCC-CC	15.0		1.5	0.90	0.75	4.2		0.15
8-5	C/L/CCC-CC	12.0*					12.0		0.12
11-8	J/S/CCDECC	1.3		0.026	0.21	0.013	0.026	0.16	0.013
11-13	J/S/CCC-CC	1.5		0.15		0.015	2.6		0.015
11-22	C/M/OOO-BC	5.5		1.7	0.05	0.55		0.55	
12-3	J/M/NEENNC	1.5		0.75	2.3	1.5	2.3		9.8
12-5	J/M/CCCCAC	2.0*		4.8	4.4		8.2	0.80	19.8
12-6	J/S/DDE-BB	0.30		0.30	0.30	0.015	0.30		0.06
12-8	C/M/CCCCCC	1.1	26	0.77	0.22		0.66	0.66	0.11
12-9	C/S/IRI-IC	1.2		1.2	1.2		0.06	1.2	0.03
12-12	C/M/---EE-	0.35							0.35
13-2	C/M/COI-CC	0.77		2.3	1.9			0.22	0.77
15-1	C/M/---EE-	0.64						3.2	1.9
19-2	J/S/LCLLLC	1.2				0.036	0.38		1.2
19-3(b)	J/S/--I--C	0.07		0.01	0.01	0.028	0.046	0.008	
20-1	C/S/C-CCCC	12.0	156	2.2		0.36		15.6	0.72
20-6	C/S/CCB-BC	0.77		0.074	0.30	0.12	0.77		0.008
20-7	C/S/CCBCBC	2.1	53	0.21	1.5	0.021	0.42	0.53	0.021
20-10	C/M/-II--C	0.55			1.1		1.1		
20-13	C/S/ICIIIC	3.1		0.31	0.93		0.31	0.62	0.31
20-15	C/M/-BB--B	7.7			7.7		7.7		
20-17	C/S/CCCCCC	2.0	42	0.82	0.96	0.10	0.66	0.16	0.003
21-3	C/S/BBBBBB	5.9		1.2	1.5		1.2	0.18	0.059
23-3	J/M/CCC-CC	6.4*		11.0			64.0	13.0	1.3
25-1	C/M/CCCCCC	0.73		0.051	0.58		0.11	0.64	0.022
28-9	J/L/-B--BB	0.14*		1.4					0.0014
28-11	C/M/CCCCCC	1.3	20	0.53	0.65	0.20	1.6	0.50	0.065
30-1	J/M/LCLLLC	1.5		0.30	11	0.015	7.5	12	0.53
30-5	C/S/IIIIIC	9.1		1.8	1.8	0.41	6.8	4.1	0.46
30-7	C/S/III-IC	0.44		1.5					
30-8	C/M/--NBBB	4.2					4.2	21	0.17
33-1	J/S/CCCCCC	0.65	14	0.13	0.20	0.039	0.20	0.52	0.085
33-2	C/S/BNN-NB	34*	323	50	34	0.51	4.8		19
33-3F	C/M/--IEEC	1.6					0.08	0.08	0.21
33-3U	C/M/--IEEC	1.1					0.06	0.06	0.14
33-6	J/M/CCC--C	0.86	7.3	0.086	0.043	0.43			
33-8(c)	C/S/--B--B	132					6.6		
33-9	J/M/NDD-NC	0.40	3.8	0.052	0.64	0.15	0.21		
33-11	C/M/C-CCCC	0.77		2.4		0.46	1.4	0.39	0.0077
33-15	C/S/CCB-BC	0.64	13	0.13	0.27	0.026	0.15	0.06	0.016
33-20	C/M/CCCCCC	1.9		0.40		0.37	0.52	0.95	0.015
33-21	C/M/--CCCC	2.5	265	0.30	0.75	0.10	0.28	2.1	0.13
36-1	C/S/BBBBBB	2.3		0.023	0.023		0.14	0.32	0.023
36-2	C/M/INI-IB	2.4		0.38	18	0.072	0.072	0.31	0.048
40-4	C/S/DDD--C	0.64		1.3	3.2		0.64		
43-1	C/S/RCRBBB	0.08		0.023	0.028		0.024		0.0008

(a) An asterisk after the water use means that calculations were based on an assumed 8-hour work day.

(b) Hard chromium only; multiply numbers by 50. No chromium was expected in effluent.

(c) Hard chromium only; multiply numbers by 50. Large water addition prior to treatment.

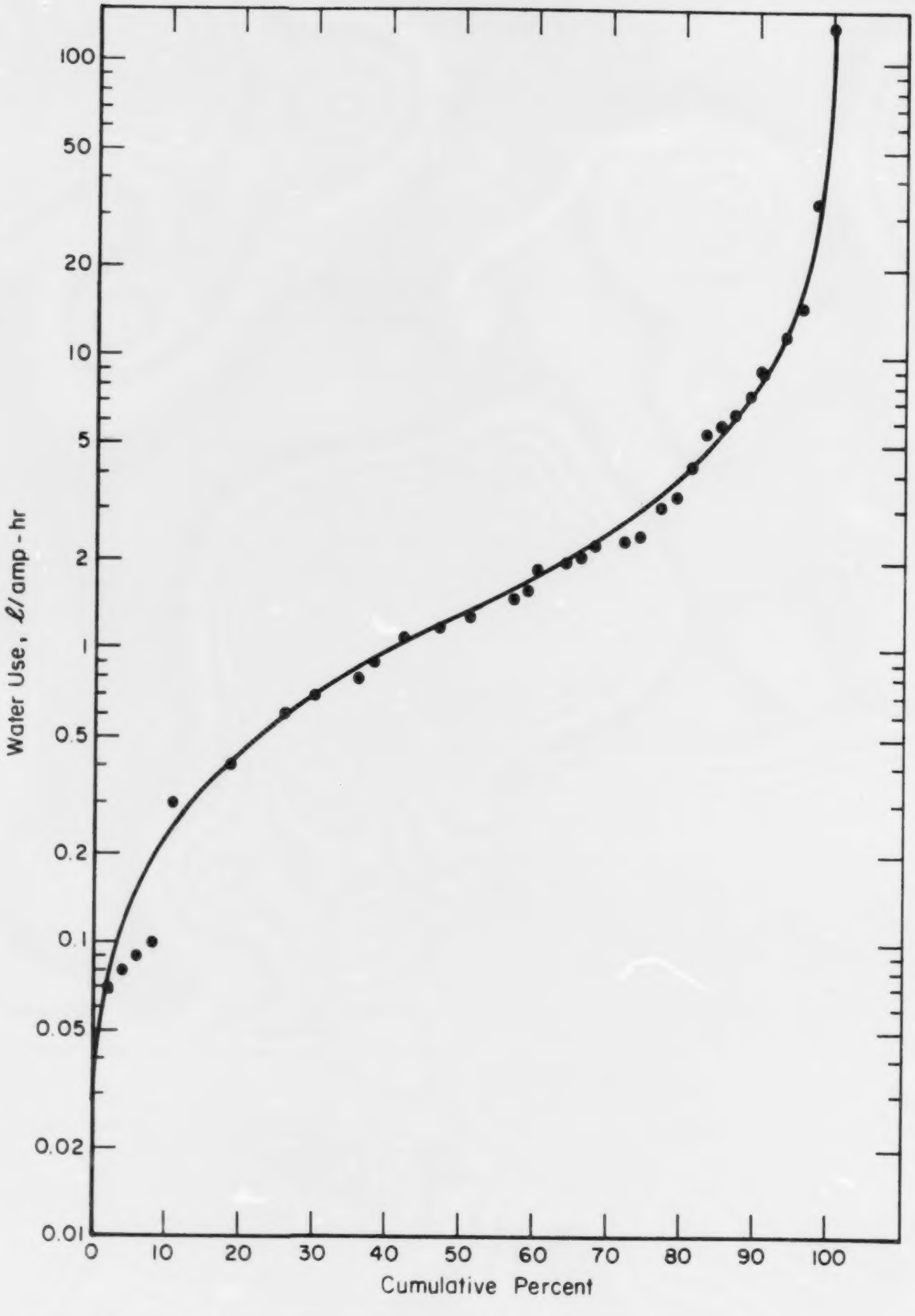


FIGURE 23. WATER USE BASED ON TOTAL INSTALLED CURRENT VERSUS CUMULATIVE PERCENTAGE OF 53 PLANTS

A comparison of the above values with those in Table 29 shows that many plants attain lower values for a single pollution parameter. However, for all pollution parameters (all metals and cyanide) the above values are attained by only 11 plants in Table 29 (3-1, 3-3, 3-4, 11-8, 12-6, 19-3, 25-1, 33-1, 33-15, 36-1, and 43-1).

Four of these plants were chosen for further study. Figure 24 shows that those plants (15) that are using some combination of in-process control for chemical recovery (evaporation, ion exchange, reverse osmosis) in one or more plating operations have lower water use than those plants (38) that do not use such in-process controls. The apparent two-to-three-fold reduction is water use in probably indicative of the general use of multitank countercurrent rinsing and other water conservation practices in these plants.

Figures 25 through 31 show the data of Table 29 on performance being obtained by various plants separately for each parameter: copper, nickel, hexavalent chromium, total chromium (Cr^{+3} + Cr^{+6}), zinc, cyanide (amenable to oxidation by chlorine) and suspended solids. For a general estimate, a value of 40 to 80 AH/sq m can be used to convert waste discharged from mg/AH to mg/sq m and water use from kg/AH (or 1/AH) to kg/sq m (or 1/sq m). A value of 60 AH/sq m corresponds to the following thicknesses of the various plated metals:

Metal	Cur Eff. %	mils
Cu	100	0.31
Ni	100	0.29
Cr	13	0.014
Zn	60	0.24

The various waste management technologies were identified by symbols in Figures 25 through 31. The appropriate symbol is used for each parameter to show whether a reduction in quantity of waste discharged was achieved as the result of using the particular technology.

Continuous (flow through) chemical treatment is the baseline technology for reference with inplant segregation of chromium and cyanide streams for separate treatment prior to recombination with the remaining waste streams (acid/ alkali and others) for final separation of precipitated metals. The use of this technology provides the best overall results for all parameters because its use insures complete treatment of the acid/alkali stream to remove precipitated metal.

Complete batch chemical treatment of all segregated streams is an alternative to continuous chemical treatment that can provide equivalent pollution reduction. Batch chemical treatment of only the hexavalent chromium and cyanide streams (Figure 16 and 19) combined with continuous chemical treatment for metal removal

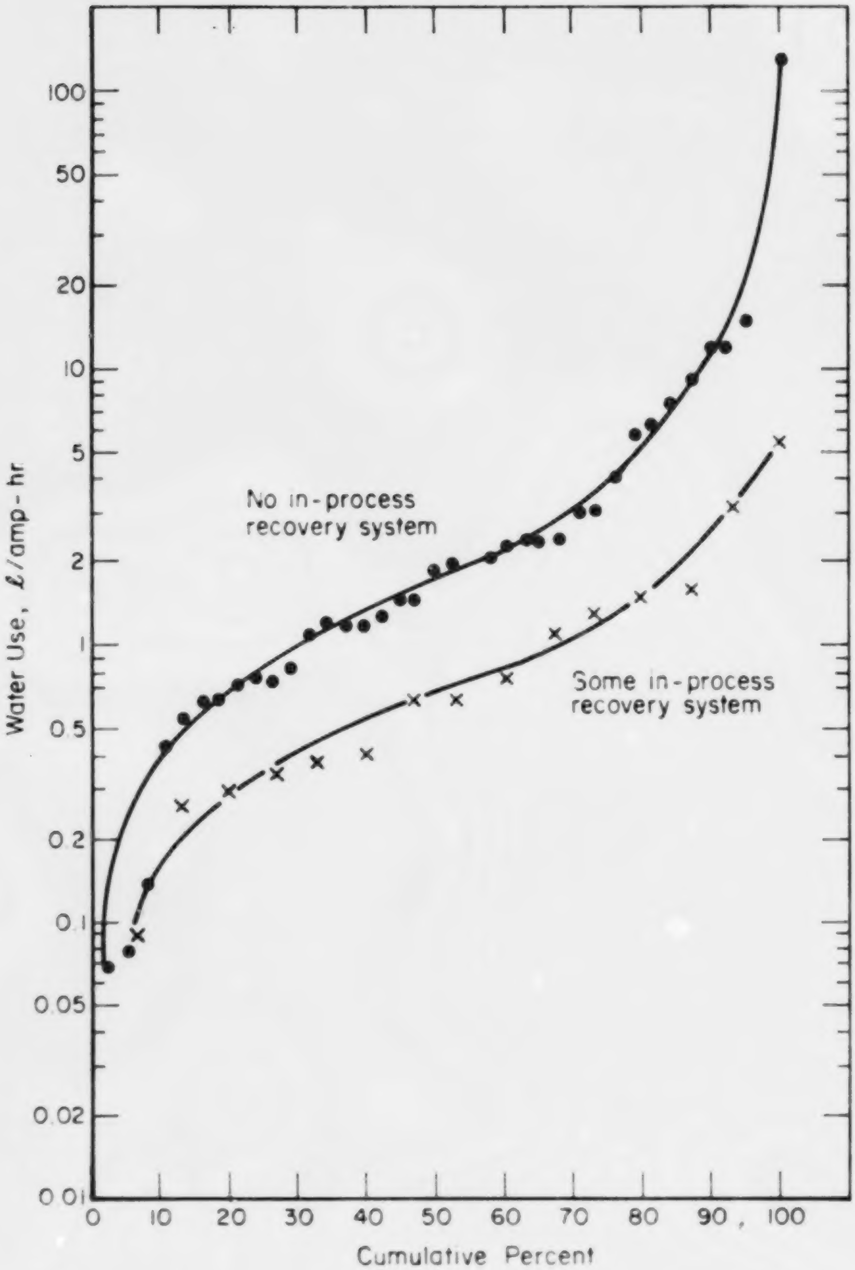


FIGURE 24 COMPARISON OF THE WATER USE FOR PLANTS THAT USE IN-PROCESS CHEMICAL RECOVERY SYSTEMS ON ONE OR MORE PLATING OPERATIONS WITH THE WATER USE OF PLANTS THAT DO NOT USE IN-PROCESS RECOVERY

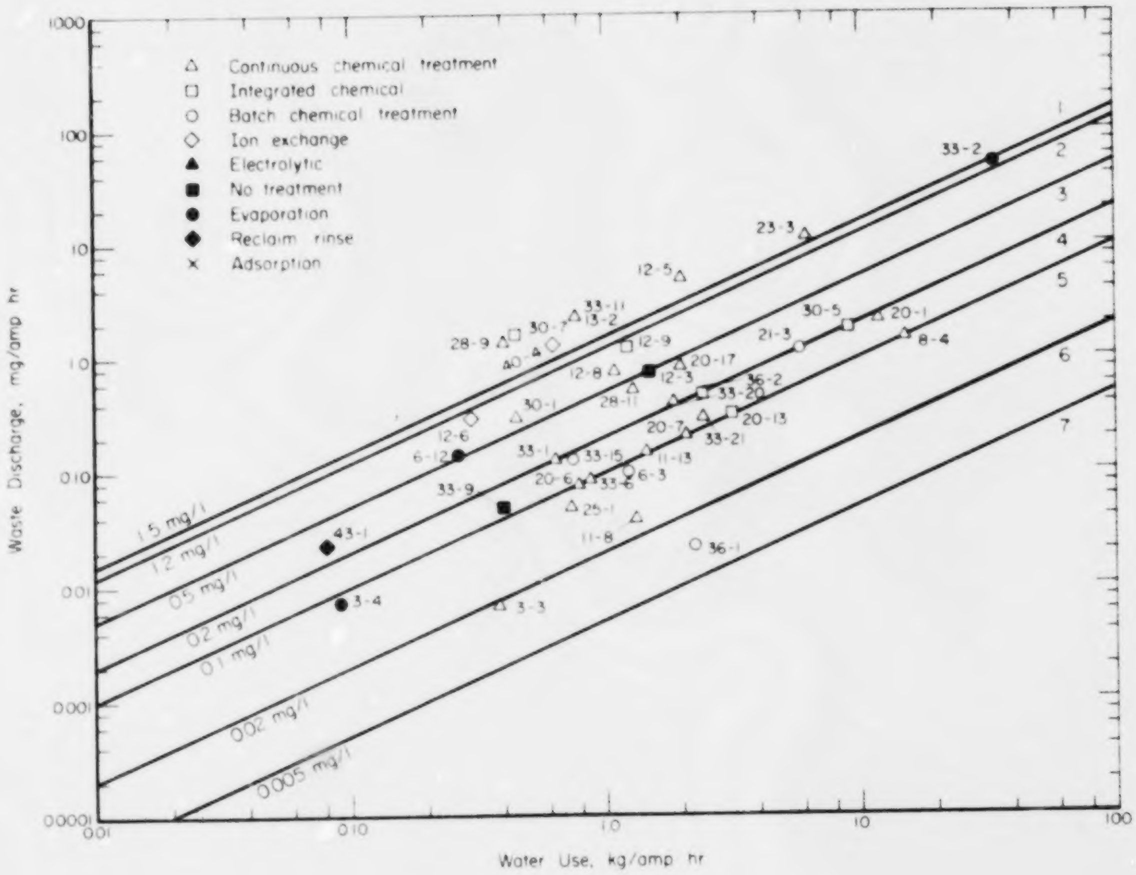


FIGURE 25 . COPPER IN TREATED EFFLUENT FROM ELECTROPLATING

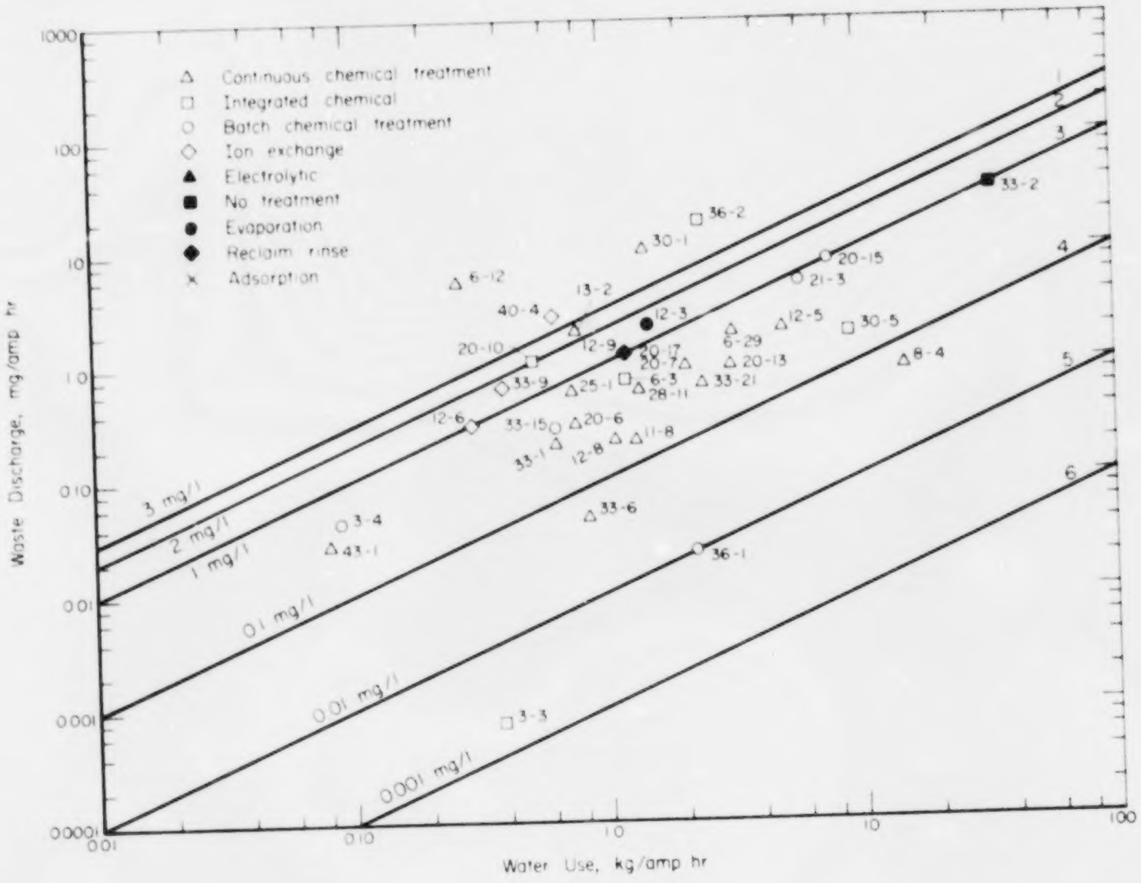


FIGURE 26. NICKEL IN TREATED EFFLUENT FROM ELECTROPLATING

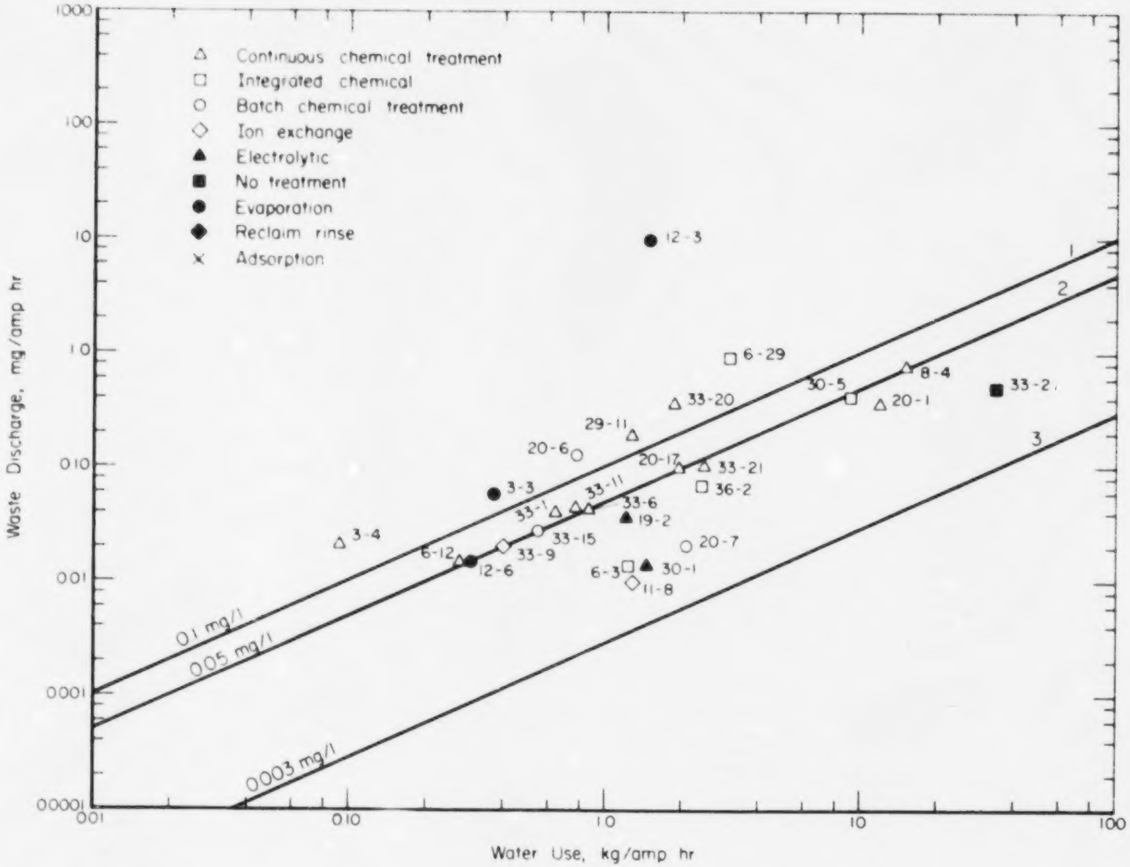


FIGURE 27. HEXAVALENT CHROMIUM IN TREATED EFFLUENT FROM ELECTROPLATING

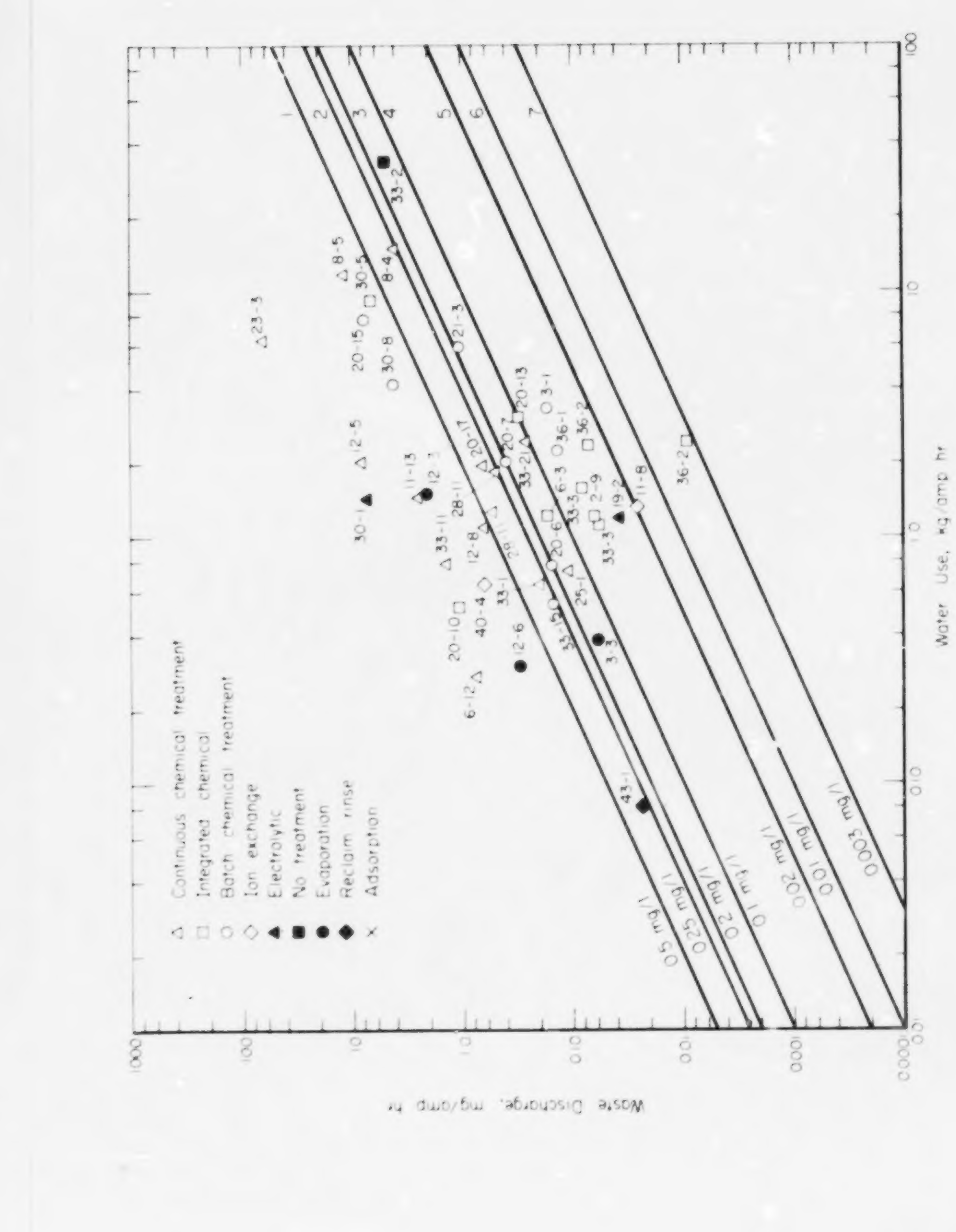


FIGURE 28. TOTAL CHROMIUM IN TREATED EFFLUENT FROM ELECTROPLATING

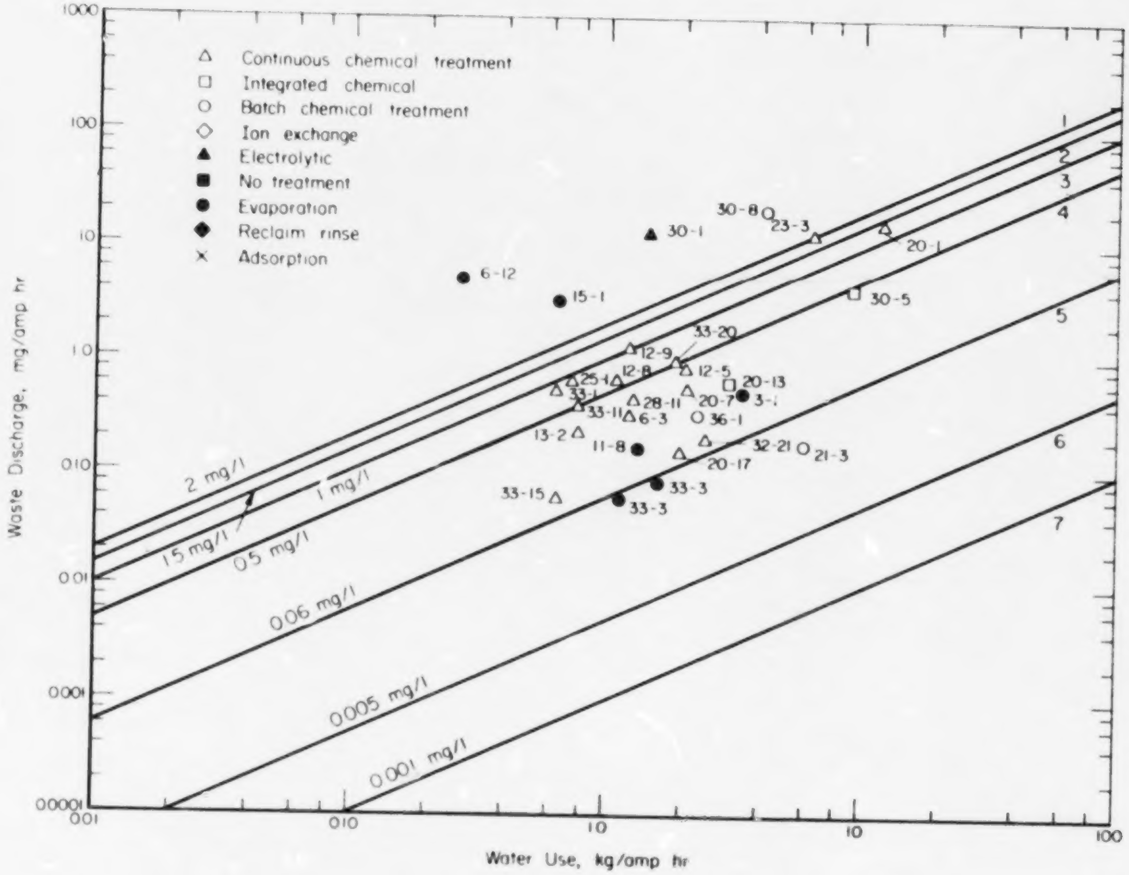


FIGURE 29 . ZINC IN TREATED EFFLUENT FROM ELECTROPLATING

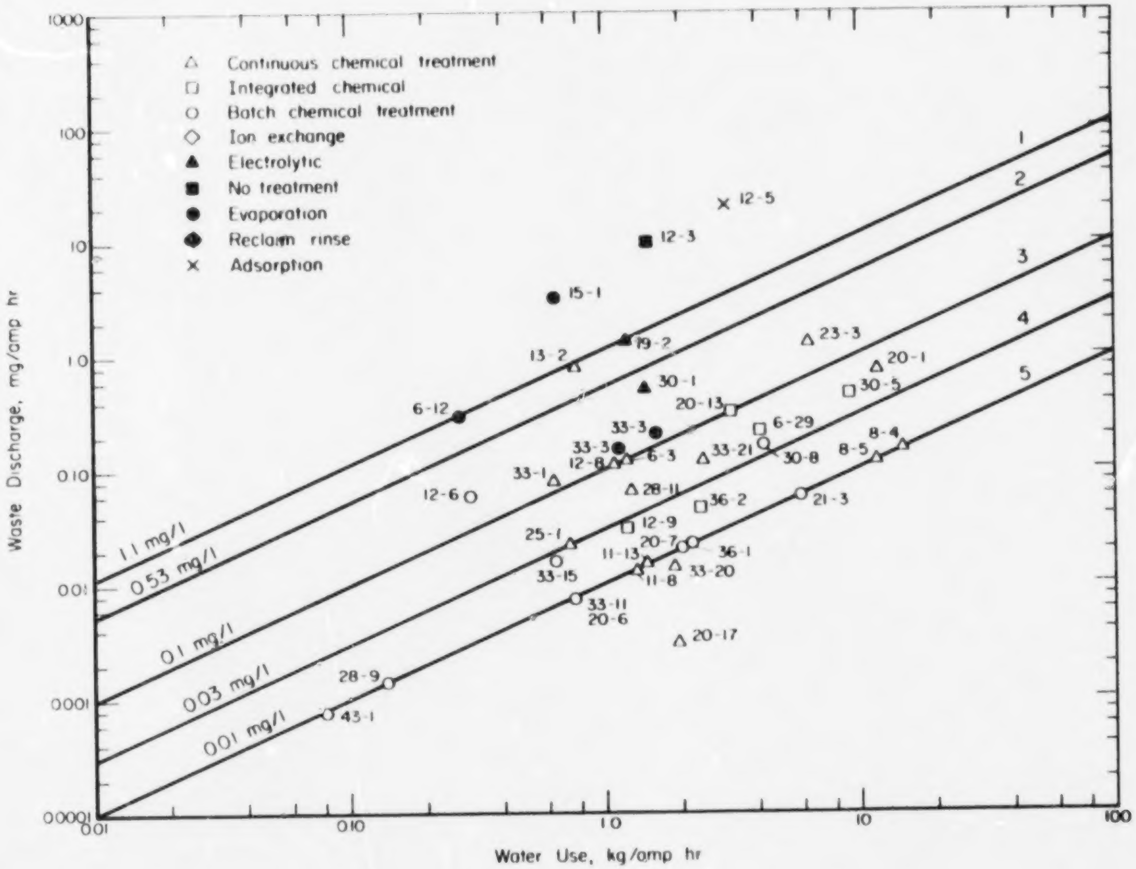


FIGURE 30. CYANIDE IN TREATED EFFLUENT FROM ELECTROPLATING

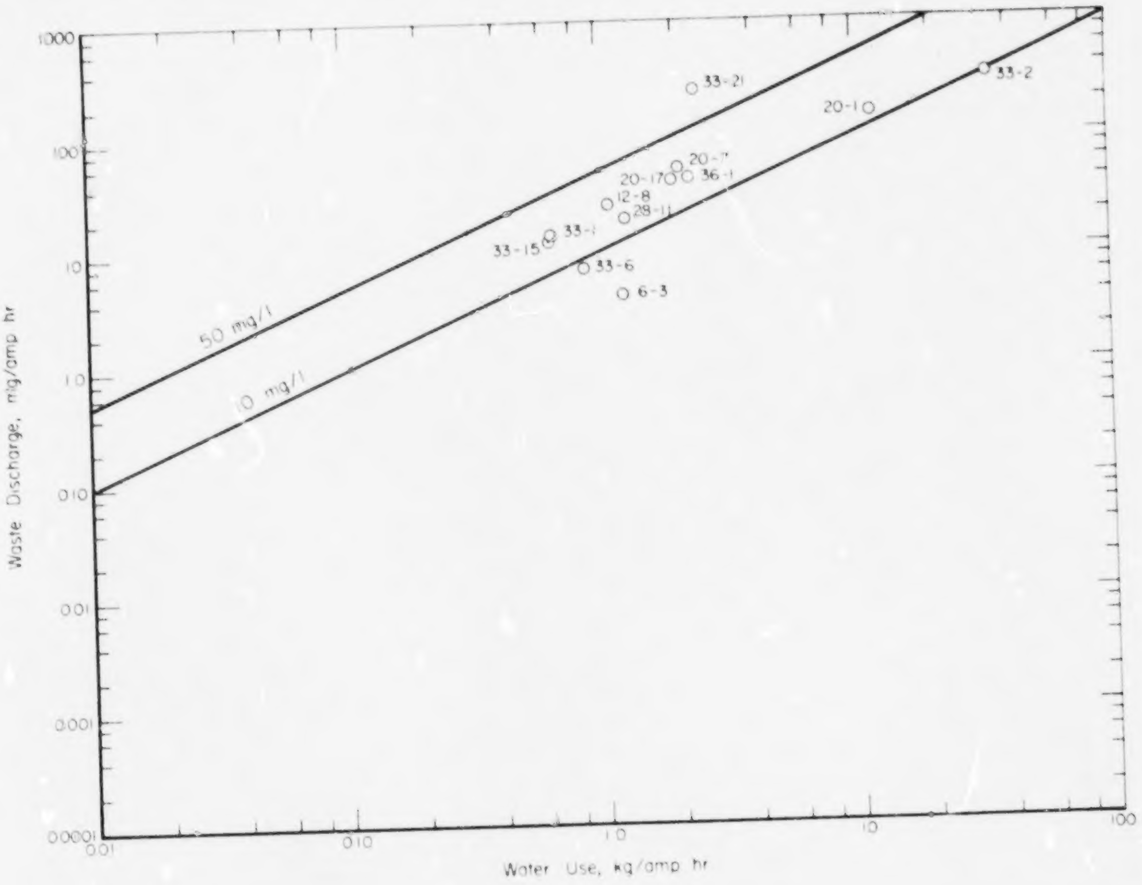


FIGURE 31 . SUSPENDED SOLIDS IN TREATED EFFLUENT FROM ELECTROPLATING does not provide significantly greater pollution reduction (Figures 14, 15, 17, and 18).

All other technologies currently in use for in-process treatment after one or more plating processes such as integrated chemical treatment, are combined with end-of-process continuous or batch treatment of at least the acid/alkali stream for removal of metals. Where there is no treatment prior to discharge beyond pH adjustment, the effluent may contain a high level of pollutants. There was no evidence from plant data that any in-process treatment achieved greater pollution reduction than that which can be achieved by end-of-process chemical treatment.

In-process controls used after plating operations for recovery of chemicals such as evaporation, ion exchange, reclaim rinses, and reverse osmosis and/or reduction of water use are combined with end-of-process chemical treatment. Without chemical treatment, the effluent may contain a high level of pollutants. Thus, there is presently no evidence that greater pollution reduction than by chemical treatment can be achieved by use of these technologies. Closing up one or all plating operations by evaporative technology does not presently succeed in eliminating the pollution parameter from the final effluent. In general, the present use of the above in-process controls does not lead to a significant reduction in pollution for the total electroplating facility which includes rinse water after pretreatment and posttreatment operations.

The above conclusions based on the degree of pollution reduction achieved by existing sources indicates that end-of-process chemical treatment in combination with in-process controls for water conservation is the Best Practicable Control Technology Currently Available for existing sources in the electroplating industry.

In using the term chemical treatment no distinction is made between continuous chemical treatment, batch chemical treatment, integrated chemical treatment or other in-process treatments or combinations provided that the effluent limitations are achieved. No distinction is made in the specific chemicals used, specific chemical reactions, or specific processes employed for destruction of cyanide, reduction of hexavalent chromium, or removal of metals provided the effluent limitations are achieved. In using the term in-process controls, no distinction is made between the various methods of recovery of chemicals or water conservation. Effluent limitations can be achieved by either reduction in water use or reduction in concentration of pollutant after final treatment or both. It is recognized that the results attainable with any waste- management technology are dependent on correct operation of the process, the maintenance of control instrumentation, and the quality and capability of operating and supervisory personnel.

Detailed Analysis of Plant Data

From the above analysis of data from 53 plants, 5 plants were selected for additional on-site detailed analysis of plating operations for correlation with in-process controls for water conservation and waste treatment results including sampling to verify effluent data reported. One of the plants selected (19-3) had only hard chromium plating operations which is a special situation because of the thick deposit. The other four plants (11-8, 12-8, 33-1, and 36-1) were selected as representative of the average of the best plants involved in rack and barrel electroplating of copper, nickel, chromium and zinc.

The data obtained from each of the four second-round plant visits were analyzed with respect to the various pertinent process lines of rack and barrel plating of copper, nickel, chromium, and/or zinc. Non-pertinent process lines (e.g., anodizing, bright dipping, cadmium plating, or other than rack and barrel plating) were not included as well as certain pertinent process lines not in use or for which insufficient data were available. The composite of the pertinent lines was also analyzed. The purpose of the analysis was to study water use.

The various factors based on the composite of process lines are shown in Table 30. The monthly average concentration of each pollutant parameter reported by the plant multiplied by the specific water use (l/AH) or effluent factor (l/sq m) yields the waste discharge in mg/AH or mg/sq m respectively as shown in Table 31. The values can be compared to the recommended 1977 effluent limitations for existing sources for copper, nickel, chromium (total), zinc, and total cyanide (80 mg/sq m) and for hexavalent chromium and oxidizable cyanide (8 mg/sq m) and for suspended solids (2400 mg/sq m).

For comparison, the corresponding data using the results of sampling and analysis on the day of the plant visit and the appropriate water use factors from Table 30 are shown in Table 32.

For plants required to analyze daily composite samples for monthly reporting to authorities, the monthly averages over a prior period of 6 to 12 months were used to determine typical average concentrations of pollutants. In general, the latter value is more representative of waste treatment results than samples obtained over a short period during a plant visit. However, for Plant 33-1, the average results for 1972 were considerably higher than those obtained after about June 1972, as shown in Table 33. A significant reduction in concentration of metals occurred coincident with reduction of suspended solids concentration as a result of improved clarification. The concentrations currently achieved in 1973 are lower than the average values used previously in Table 31 to determine mg/AH and mg/sq m for each pollutant parameter.

Daily variations in concentrations of metals and cyanide in treated effluent compared to the monthly average are to be expected. Figure 32 shows the typical variation in analysis of

TABLE 30. SUMMARY OF WATER USE PARAMETERS FOR FOUR PLANTS BASED ON COPPER, NICKEL CHROMIUM OR ZINC PLATING AND EXCLUDING NON-PERTINENT METAL FINISHING PROCESSES

Company No.	Specific Water Use, l/AH	Effluent Factor, l/sq m	Coulombic Equivalent Factor, AH/sq m
11-8	2.44	170.3	69.7
12-8	1.77	95.5	53.7
33-1	1.34	77.3	57.6
36-1	1.08	114.0	105.6
average	1.66	114.3	71.7

TABLE 31. SUMMARY OF TREATED EFFLUENT FROM COPPER, NICKEL, CHROMIUM OR ZINC EXCLUDING NON-PERTINENT PLANT METAL FINISHING OPERATIONS

Pollutant Parameter	Plant 11-8	Plant 12-8	Plant 33-1	Plant 36-1	Average
Cu					
mg/l	.03	.70	.20	.03	.24
mg/AH	.07	1.24	.27	.03	.40
mg/sq m	5.1	66.8	15.5	3.4	22.7
Ni					
mg/l	.16	.20	.30	.02	.17
mg/AH	.39	.35	.40	.02	.29
mg/sq m	27.2	19.1	23.2	2.3	18.0
Cr(Hex)					
mg/l	.01	--	.06	.01	.03
mg/AH	.02	--	.08	.01	.04
mg/sq m	1.7	--	4.6	1.7	2.7
Cr(Tot)					
mg/l	.02	.60	.31	.06	.25
mg/AH	.05	1.06	.42	.06	.40
mg/sq m	3.4	57.3	24.0	6.8	22.9
Zn					
mg/l	.12	.60	.80	.14	.41
mg/AH	.29	1.06	1.07	.15	0.64
mg/sq m	20.4	57.3	61.9	16.0	38.9
CN(Ox)					
mg/l	.01	.01	.13	.01	.06
mg/AH	.02	.18	.17	.01	.10
mg/sq m	1.7	9.6	10.0	1.1	5.6

TABLE 32. SUMMARY OF TREATED EFFLUENT SAMPLING AND ANALYSIS DURING SECOND ROUND VISIT FOR COMPARISON WITH TABLE 2

Pollutant Parameter	Plant 11-8	Plant 12-8	Plant 33-1	Plant 36-1	Average
Cu					
mg/l	.07	.33	.46	3.16	.29
mg/AH	.17	.58	.62	3.41	.46
mg/sq m	12	31	36	360	26
Ni					
mg/l	.54	.17	.22	.44	.34
mg/AH	1.32	.30	.29	.47	.60
mg/sq m	92	16	17	50	44
Cr(Hex)					
mg/l	.15	.65	.05	.05	.22
mg/AH	.37	1.15	.07	.05	.41
mg/sq m	25	62	4	6	24
Cr(Tot)					
mg/l	.33	1.33	.20	.28	.54
mg/AH	.80	2.35	.27	.30	.93
mg/sq m	56	127	15	32	57
Zn					
mg/l	.49	.42	.90	.66	.62
mg/AH	1.20	.74	1.21	.71	.96
mg/sq m	83	40	70	75	67
CN(Tot)					
mg/l	.78	.22	.21	.13	.33
mg/AH	4.64	.39	.28	.14	1.36
mg/sq m	133	21	16	15	46
SS					
mg/l	--	24	22	20	22
mg/AH	--	42	29	22	31
mg/sq m	--	2292	1701	2280	2091

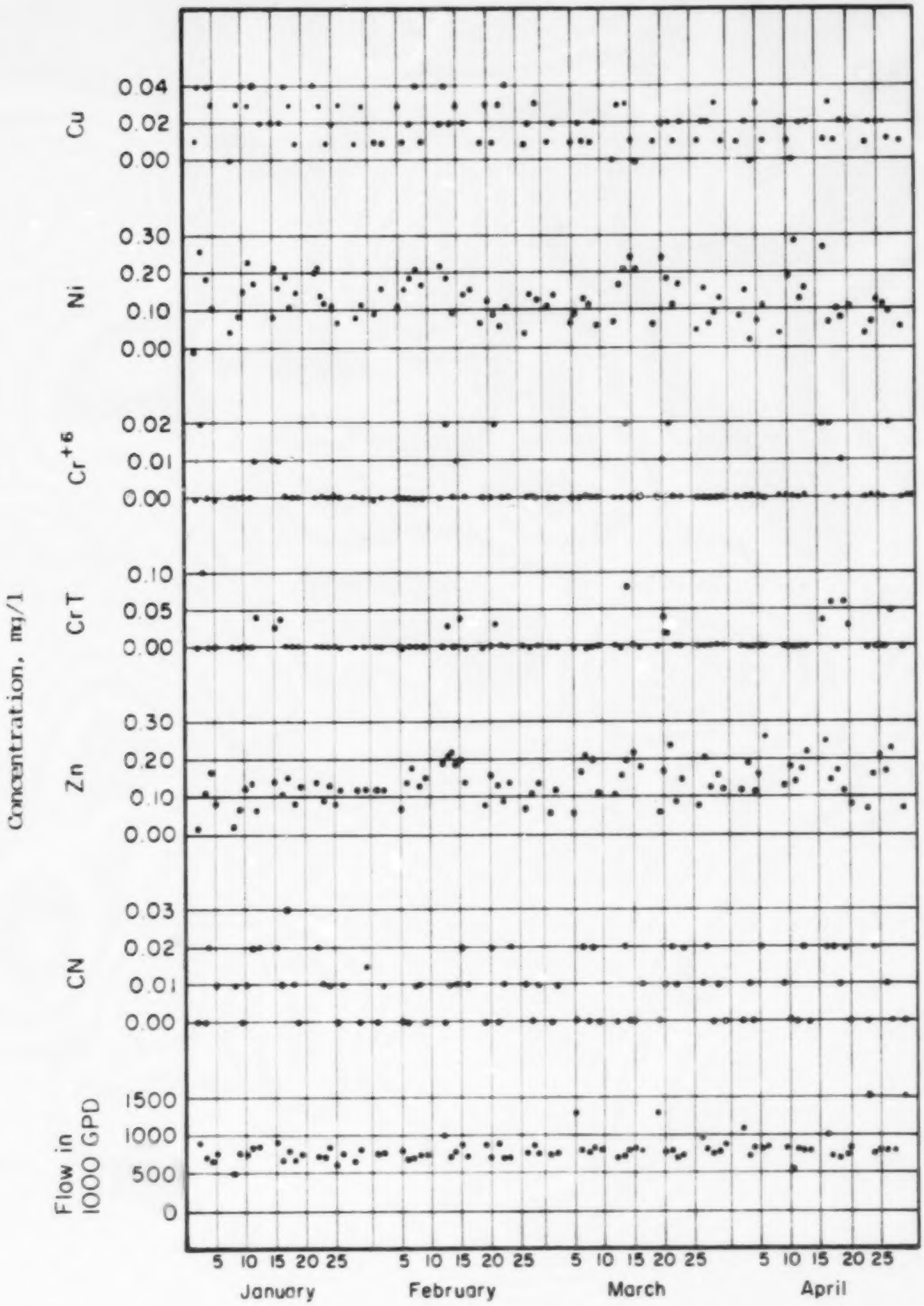


FIGURE 32. TYPICAL VARIATION IN CONCENTRATION OF POLLUTANT PARAMETERS FROM ANALYSIS OF DAILY COMPOSITE OVER A 4-MONTH PERIOD REPORTED BY PLANT 11-8

daily composites over a 4-month period for Plant 11-8. Because of the low concentrations being measured, daily concentrations are at times twice the monthly average concentration. One factor is analytical accuracy. For example, in the measurement of copper (1 mg/l), chromium (0.05 mg/l) and zinc (0.5 mg/l) by atomic absorbtion methods the relative standard deviations are 11, 26, and 8 percent respectively (4). Another factor is that daily composite samples are usually analyzed the day following collection. Thus, there is a 24-hour time lag in detection of slight changes in waste treatment performance before corrective action is taken. In view of the above factors and determination of plated area, effluent limitations should be based on cumulative 30-day averages with an allowance for daily maximums exceeding the 30-day average by a factor of 2.

Determination of Effluent Limitations

The quantitative effluent limitations based on Best Practicable Control Technology Currently Available for existing sources discharging to navigable waters to be achieved by 1977 were listed in Table 1. The quantitative values were based on determination of what can be achieved by the average of the best plants in the electroplating category. The values are based on technical consideration of what concentrations of pollutants in the treated effluent can be achieved by chemical treatment and technical consideration of what reduction in water use for rinsing can be achieved by normal practice by existing sources in the electroplating industry. The basis for the 30-day effluent limitations will be reviewed first considering the heavy metal pollutants.

For copper, nickel, total chromium, and zinc it is possible to achieve 80 mg/sq m as was shown for the average of four plants analyzed in detail. In addition, the average of the median values for copper, nickel, chromium, and zinc for 53 plants is about 0.3 mg/l. Thus, the effluent limitations can be met with an effluent factor as high as 267 l/sq m. The median water use of 53 plants was shown to be about 1.3 l/AH based on rated current or about 2 l/AH based on typical current used. Thus, a coulombic factor of 60 AH/sq m based on typical deposit thicknesses indicates an effluent factor of 120 l/sq m.

Water use less than 120 l/sq m can be achieved using good rinsing practice. For example, an automatic copper, nickel, chromium rack plating operation with 22 l/sq m and two different zinc platers (with chromate conversion) achieved 45 l/sq m. The above values were attainable by use of good in-process control without the use of any advanced recovery techniques.

Allowing for the fact that all existing sources may not be able to use optimum water conservation because of space limitation for additional rinse tanks, a value of 160 l/sq m appeared to be broadly applicable. Thus, the combination of an effluent volume of 160 l/sq m and a concentration of 0.5 mg/l for copper, nickel, total chromium, and zinc, a concentration of 0.05 mg/l of hexavalent chromium and oxidizable cyanide and a concentration of 15 mg/l of total suspended solids appeared to be technically achievable. Tentative effluent limitations, consisting of the products of 160 l/sq m and the concentrations, may then be listed as follows:

Cu	80 mg/sq m
Ni	80 mg/sq m
Cr (total)	80 mg/sq m
Zn	80 mg/sq m
Cr (hexavalent	8.0 mg/sq m
CN^- (oxidizable)	8.0 mg/sq m

To test how many of the 53 plants would be in compliance with these tentative effluent limitations, the values in Table 29 for various constituents (except TSS) in mg/AH were multiplied by 60 AH/sq m to give products in units of mg/sq m that could be directly compared with the above values. The result of this analysis was that plants could meet the effluent limitations without questions, plants could meet the guidelines for the constituents reported, but did not report all of the constituents that should have been present in their effluent. Plant 33-1 of the four pertinent plants studied in detail (Table 31) met the tentative effluent limitations compliances for various values of effluent limitations were studied and results are summarized in Table 33.

The effluent limitations of 80 mg/sq m for copper, nickel, total chromium and zinc and of 8.0 mg/sq m for hexavalent chromium and oxidizable cyanide are achieved by at least 10 plants according to the reported data. The verification data obtained indicate that at least two plants (33-1 and 11-8) can achieve these limitations. The limitations are achieved through water conservation and treatment of waste water to yield low concentrations of these components with effluent. The achievement of these effluent limitations by these plants constitutes the basis for preparing them for standards to be achieved by 1977.

The effluent limitation for total cyanide of 80 mg/sq m was based on a concentration of 0.5 mg/l combined with an effluent factor of 160 l/sq m. Some plants may analyze for total cyanide and report the value simply as cyanide meaning maximum oxidizable as well as total cyanide. However, some plants report oxidizable cyanide only. The average value determined by analysis of samples from the four plants tudied in detail was less than 0.5 mg/l total cyanide. Three of the four plants had 20 mg/m^2 or less.

The effluent limitation for total suspended solids of 2400 mg/sq m was based on an effluent factor of 160 l/sq m combined with a concentration of 15 mg/l achieved by over half of the plants for which data was available. The value for three plants during visits was 22 to 24 mg/l representative of a single day.

TABLE 33. COMPLIANCE OF ELECTROPLATING FACILITIES WITH EFFLUENT LIMITATIONS GUIDELINES

Effluent Limitation - Cu, Ni, CrT, Zn mg/sq m/op	30 Day Average Cr^{+6}, oxidizable CN mg/sq m/op	No. of plants meeting guidelines on basis of industry data	Additional plants meeting guidelines but lacking some data	Plants verified meeting guidelines
40	4.0	5 (3-1, 3-3, 11-8, 25-1, 36-1)	4 (3-4, 12-6, 33-15, 43-1)	1 (33-1)
60	6.0	6 (above + 33-1)	4 (above)	1 (above)
80	8.0	10 (above + 6-3, 12-8, 12-9, 20-10)	5 (above + 20-6)	1 (above)
100	10.0	13 (above + 20-7, 28-9, 30-7)	8 (above + 21-3, 33-30, 33-9)	1 (above)
120	12.0	15 (above, + 20-7 28-11)	8 (above)	1 (above)

TABLE 34 MONTHLY AVERAGE EFFLUENT CONCENTRATION FOR PLANT 33-1 SHOWING IMPROVED RESULTS OBTAINED OVER A 14-MONTH PERIOD

			Chromium								
Year	Month	Cd	Cr^{6+}	Cr^{3+}	Cu	Fe	Ni	Zn	CN	S.S.	pH
1972	Jan.	0.31	0.08	1.07	1.6	--	--	5.6	0.08	18.9	7.5
	Feb.	0.28	0.15	1.45	0.80	--	--	16.0	0.08	32	7.6
	Mar.	0.26	0.12	0.08	1.3	--	--	24.0	0.09	52	7.2
	Apr.	0.54	0.05	0.70	1.30	--	--	8.50	0.06	27.50	8.3
	May	0.15	0.05	0.30	1.10	--	--	2.40	0.06	12.0	8.4
	June	0.03	0.04	0.16	1.0	--	--	0.2	0.12	8.0	8.9
	July	0.07	0.04	0.16	0.30	0.30	0.30	0.20	0.10	10.0	8.4
	Aug.	0.03	0.04	0.26	0.60	0.20	0.60	0.20	0.11	10.0	8.1
	Sept.	0.03	0.05	0.15	0.80	0.20	0.60	0.20	0.10	10.0	8.9
	Oct.	0.01	0.03	0.07	0.20	0.10	0.80	0.10	0.10	15	8.8
	Nov.	0.01	0.05	0.05	0.20	0.30	0.70	0.20	0.02	11	8.5
	Dec.	0.18	0.03	0.05	0.15	0.20	0.20	0.20	0.02	12.4	7.9
1973	Jan.	0.05	0.01	0.06	0.10	0.20	0.20	0.10	0.02	11.1	7.6
	Feb.	0.05	0.02	0.10	0.03	0.08	0.10	0.09	0.01	8.9	7.8
	Mar.	0.05	0.01	0.02	0.09	0.09	0.10	0.03	0.01	11.0	7.9
	Apr.	0.09	0.02	0.03	0.07	0.20	0.06	0.20	0.02	11.6	7.7

(1) Averaged concentrations for each month are in mg/l for daily composite analysis of waste water.

A 9-month average value of about 10 mg/l achieved by one of the plants was considered representative.

The above values used in determining effluent limitations a summarized in Table 36 in terms of concentration of the polluta parameter in mg/l for selected effluent factors in 1/sq m, t product of which corresponds to the effluent limitations of Tab 1 in mg/sq m. The concentrations of Schedule A and B in t interim guidelines for the electroplating industry as shown f comparison. In general, the concentration values of Schedule are similar to those for an assumed effluent factor of 80 1/sq The latter values on which effluent limitations are bas represent what is technically achievable; the desired values Schedule A were derived with consideration of water quality a stream standards.

The effluent limitations for BPCTCA in Table 1 are based on tota metal rather than dissolved metal for several reasons, bu principally because insoluble metal hydroxides can redissolv depending on the pH of the receiving body of water. The need t limit insoluble metal in the effluent has been recognized for long time (e.g., the limit of 1/mg/l for insoluble metal for Cu Ni, Zn and 0.25 mg/l for Cr in Schedule A). This is the reaso that good clarification and separation of suspended solids prio to stream discharge has been practiced for many years. Since th plant effluent is usually discharged at the same pH tha clarification occurs, the soluble metal concentration wil usually be significantly less than the total metal concentration. Analysis for total metal only reduces the expense of plant monitoring of the effluent discharge.

Additional Factors Considered in Selection of Best Practicable Control Technology Currently Available

Total Cost of Application of Technology in Relation to Effluent Reduction Benefits

Based upon information contained in Section VIII of the report, the average cost of chemical treatment prior to discharge of effluent to surface waters from medium sized and large plants, is $10.70/100 sq m. (9.9/1,000 sq ft). This cost averages 4 percent of the plating cost and normally will be less than 5 percent of the plating cost for most plants. The application of this technology can achieve an 85 to 99 percent reduction in pollutants in the effluent discharged to surface waters.

Cost of chemical treatment in small plants are greater than $10.70/100 sq m (9.91/1000 sq ft) as indicated in Table 22.

Cost for small plants increase as size decreases because there is a minimum capital investment ($50,000) for a chemical waste treatment facility.

TABLE 35 COMPARISON EFFLUENT LIMITATIONS FOR BPCTCA (TABLE I) IN TERMS OF CONCENTRATION FOR VARIOUS FACTORS WITH THE PRIOR INTERIM GUIDELINE CONCENTRATIONS

	Concentration(a), mg/l				
	Effluent Factor(b), l/sq m				
Parameter	40	80	160	Schedule A (c)	Schedule B(c)
Cu	2	2	.5	1.2(0.2)	1.5(0.5)
Ni	2	2	.5	2.0(1.0)	3.0(2.0)
Cr^{6+}	0.2	.1	.05		0.1
Cr_T	2	.1	.5	0.25(0.1)	0.5(0.2)
Zn	2	1	.5	1.5(0.5)	2.0(1.0)
CN,oxid.	0.2	.1	.05	0.03	0.1
CN, total	2	1.	.5	0.5	1.0
TSS	60	30	15	10	50

(a) Total metal (soluble metal in parenthesis for Schedules A and B).

(b) The product of the assumed effluent factor and concentration is the effluent limitation in mg/sq m.

(c) Schedules A and B interim guidelines for the electroplating industry.

Size and Age of Equipment and Facilities

The size of the electroplating facility in terms of surface area plated or the ampere-hours used does not affect the raw waste load concentration and the degree of pollution reduction attainable by application of the waste-treatment technology. The cost of applying the technology is not significantly different when expressed as percentage of plating costs for a wide range of plant sizes with the exception of the very small plants discussed above.

Age of waste-treatment facilities is a factor that will affect the capital cost outlay. This will be greatest for those plants not presently treating waste prior to discharge to surface waters. Modest investments will be required to update some existing treatment facilities to meet the effluent limitations. Recently constructed or updated facilities might not require any further capital investment. Some small increase in operating costs may be required to achieve the effluent limitations but the total cost of application of the technology would not exceed that based on the average of the best plants.

Some existing sources have a large investment in automatic plating machines which are difficult or expensive to modify for installation of additional rinse tanks after pretreatment and posttreatment operations. For other existing sources where space is at a premium it might be expensive and sometimes impractical to redesign existing plating lines or redesign the entire plating facility to accommodate additional rinse tanks for optimum water conservation on all operations. For these reasons, extending in-plant controls for water conservation to closed-loop operation and/or multitank rinsing following alkaline cleaners and acid dips was not considered practicable for all existing sources. Without such currently available in-process controls to reduce rinse water usage, other advanced technology designed to close up the plant with complete reuse of water to achieve no discharge of pollutants cannot be considered for existing sources except in special situations. It should be noted that limitations of space for sufficient rinse tanks would not apply to design of a new plating facility. Also, the limitations of space within existing automatic machines as older eqiupment if retired over the future years. Thus, age of equipment and facilities is a factor that influences what is practical to accomplish over the years.

Because of the above factors, Best Practicable Control Technology Currently Available for existing electroplating facilities in the industry would not eliminate discharge of pollutants.

Processes Employed

The possible variations in electroplating processes within a single existing facility were also considered. Complete segregation of single-metal waste streams was not considered practical, based on spatial limitations and economics. Stream integration dilutes one process wastewater with at least one other. Although the total volume in which a specific waste water constituent is present can thereby be increased so that the total amount dissolved is increased, the solubility is still so low that the constituent is still removed to a very high degree by precipitation and clarification.

In defining the Best Practicable Control Technology, no special allowance was made for variations in product design or shape factor. If the shape of the parts being plated requires the use of in-process controls such as countercurrent rinsing, evaporation, or other advanced recovery systems for achieving reduced water use to counteract the effect of unusually high dragout, any supplemental cost should be added to the cost of plating. Any such incremental increase in the cost of plating will direct attention to the design of parts that drain more easily to reduce dragout. This rationale of shifting the added cost, if any, of increased pollution control to the electroplating process simplifies the application of effluent limitations and places it on an equitable basis. However, provision has been made for specific modification in effluent limitations upon proof of need for exceeding the volume of water flow reflected in these recommended guidelines due to excessive dragout that is not amenable to available control technology discussed in Section VII. It is not the intent that the recommended guidelines be inflexible with regard to the shape factor such that exorbitant treatment costs would be required. Nor was it intended to deprive the public of electroplated products it needs. Permission to exceed effluent limitations should be granted in cases where high dragout caused by unusual shape complexity is not amenable to handling with current available technology with equipment available to a specific plant pending new product design to minimize the shape factor and/or equipment modification.

Engineering Aspects of the Application of Various Types of Control Technology

Advanced in-process controls for recovery of plating chemicals are rapidly gaining acceptance and often show a net cost savings compared to chemical treatment. However, the applicability of these in-process controls is dependent on first achieving reduction in water use by multitank countercurrent rinsing.

Process Changes

Process changes are not currently available to the electroplating industry that would lead to greater pollution reduction than can be achieved by the recommended effluent limitations. Some possible process changes such as use of noncyanide plating baths may eliminate one pollution parameter, but do not eliminate all. They may be useful especially with regard to the smaller facilites (those plating less than 33 sq m/hr or having an installed capacity of less than 2000 amperes) for reducing the cost of meeting the effluent limitations recommended in this document.

Nonwater Quality Enviromental Impact

As discussed in Section VIII of this report, the principal nonwater quality aspect of electroplating waste treatment is in the area of solid waste disposal. Disposal of sludges resulting from metal removal by chemical treatment is a current problem in many states that have a high concentration of electroplating facilities. The problem would be partially alleviated by disposal of drier sludge. Such added costs for removal of water from sludge would be imposed by the requirements for solid waste disposal and does not directly result from the requirement for water-pollution reduction.

The use of advanced technology to recover metal plating chemicals from rinse water rather than chemical treatment which adds to the sludge is being applied in areas where the sludge-disposal problem is greatest. Further impetus in the direction of recovery rather than disposal is expected to be provided by authorities responsible for solid waste disposal. This will have an overall beneficial effect on water pollution because of the concurrent requirements for water conservation for economic application of recovery techniques.

It is estimated that many of the existing electroplating sources discharging to navigable waters are already using chemical treatment methods with a high percentage removal of metals. This is particularly true in geographic areas where water pollution reduction has been emphasized and the sludge-disposal problem is most evident. Achieving the effluent limitations by application of chemical treatment technology will have little impact in total quantity where solid waste disposal is a problem.

There will be no direct effect on air quality as a result of the application of recommended technology for water-pollution reduction. Indirect effects related to increased energy use will be minor. Energy requirements (mainly electrical) for chemical treatment are estimated to be 3.2 percent of the power needed for electroplating.

Guidelines for the Application of Effluent Limitations

Selection of Production Unit

Effluent limitations are intended to specify the maximum quantity of pollutants which may be contained in the discharged treated effluent from a point source. This quantity must be related to a unit of production so that the effluent limitations can be applied broadly to various plants in the same category regardless of their production capacity. For example, an effluent limitation for a particular wastewater constituent in mg/unit times the production rate in units/hr equals the maximum amount of that constituent that can be discharged in mg/hr. Thus, for any production unit:

$$\frac{mg}{unit} \times \frac{Unit}{hr} = \frac{mg}{l} \times \frac{l}{hr} \qquad \text{Equation 1}$$

The right-hand side of the above equation represents the normal method of monitoring based on analysis of concentration of individual pollutants in the effluent in mg/l and measurement of the effluent discharge rate in l/hr. Expressing the effluent limitation as a function of a production unit compensates for change in production rate, which changes the effluent discharge rate. The effluent rate in the electroplating industry is closely related to the rinse water rate which is in turn related to the production rate of electroplated parts.

The effluent discharge rate as volume per day is commonly reported by electroplating and other industrial sources. Because many plants do not work on a 24-hour-day basis at all times, it would be preferable to use the next smaller unit of time, which is an hour. This avoids the uncertainty associated with the daily unit which often requires further defintion as to the number of shifts worked per day and the hours per shift.

The most appropriate production unit in some industries is the weight of product produced or the weight of raw materials purchased. Niether a unit quantity of product produced nor a unit quantity of raw material use is appropriate for the electroplating industry, because the quantity of product expressed as the weight of products plated does not bear any relation to raw waste produced. Electroplating is a surface process that is not influenced by the volume or density of the part plated. The raw waste load is related to surface area (not volume) of electroplated parts which determines the concentrated solution dragout, rinse water use, and ultimately the degree of pollution reduction achievable. While it is common in barrel plating of small parts to weigh the plated parts as a control measure for basket loading, the optimum weight of parts was originally determined by trial and error plating or precalculation of the part per unit weight in order to achieve the correct total area for optimum plating current density. Regardless of the method of controlling the plating operation, the dragout is related to the total area of parts plated and not the weight. Solution adhering to the surface of small parts causes dragout. Although some cup-shape parts that are difficult to drain or rinse may cause high dragout not directly related to area, weight would not be a good unit quantity applicable to both rack and barrel plating.

Although the amount of raw material used or chemicals purchased was considered as a possible unit quantity related to production, neither unit appeared suitable as a reliable measure of production. The weight of material purchased and used as soluble anodes ends up on the parts plated, but this weight must be divided by the thickness plated to obtain a correlation with production rate in area plated per unit time which is the true determinant of raw waste load. In the case of chemicals purchased for bath make up and particularly for chromium salts purchased for plating with insoluble anodes, there is a further complication. A material balance will show that the difference between the chromium purchased and the chromium on the plated parts produced equals the chromium in the precipitated sludge minus the small amount of chromium discharged with the treated effluent. Thus, chromium in chromium salts purchased in excess of that on plated parts reflects dragout and increased sludge but not necessarily increased water pollution. The same reasoning applies to all other metal-containing chemicals purchased for bath make up which primarily end up as precipitated and separated sludge. Although the amount of chemicals purchased indicates total dissolved salts in the treated effluent, total dissolved solids is not considered an important pollutant parameter in the electroplating industry.

Consideration of the above factors led to the conclusion that the unit of production most applicable to the electroplating industry is surface area. The surface area withdrawn from a concentrated solution in a plating operation is the paramount factor influencing dragout of solution constituents, some portion of which ends up in the waste water and treated effluent. Surface area influencing dragout includes not only the surface area receiving an electroplate but also the surface area of nonsignificant surfaces receiving little or no electrodeposit plus the surface area of racks or barrels which hold the parts.

The total surface area is rarely known and impractical to measure in some cases in the electroplating industry. In this case, the plated area is the alternative logical unit of production. However, plated area is not a measurement that has been historically recorded by the industry and may not be readily available from all plants. Alternative units of production based on amperes and water use, which are more easily measured, were developed and correlated with plated area and ultimately to the total surface area in establishing effluent limitations. These alternatives means of calculating the area plated should only be used until the industry does have ample records of area plated.

Plated Area Unit of Production*

The plated area is the primary unit of production on which the effluent limitations in Table 1 are based. Plated area is defined with reference to Faraday's Law of electrolysis by the following equation:

$$S = \frac{EIT}{100\ kt} \qquad \text{Equation 2}$$

where S = area, sq m (sq ft)
E = cathode current efficiency, percent
I = current used, amperes
T = time, hours
t = average thickness of deposit, mm (mil)
k = a constant for each metal plated based on the electrochemical equivalent for metal

deposition, amp-hr/mm-sq m (amp-hr/mil-sq ft).

The numerical product of current and time (IT) is the value that would be measured by an ampere-hour meter. Values of the constant k based on equivalent weight and the valence of the metal deposited are shown in Table 35.

Average thickness can be approximated by averaging thickness measurements at several points on a single plated part, to establish the ratio of average to minimum thickness. Minimum thickness is customarily monitored to meet the specifications of purchasers of electroplated parts, based on service requirements.

This equation was used in this study to determine the plated areas per unit time in each plating operation when the only available information was the current used and the average thickness of deposit. This equation was also used as a check on estimates of surface area plated provided by the plants contacted.

To calculate the total plated area on which the effluent limitations are based for a specific plant, it was necessary to sum up the area for each electroplating process line using Equation (2). For process lines containing two or more electroplating operations (such as in copper-nickel-chromium decorative plating) the plated area is calculated by Equation (2) for each plating operation in the process. The results should be the same, since the same parts are processed through each operation. However, if the calculated plated area differed for each plating operation in a single process line, the average of the calculated plated areas for the operations was used. The sum of the plated areas for each process line is the total plated area for the plant.

Small discrepencies in the above calculation for two or more plating operations in the same process line might be related to a difference in the actual current efficiencies from those in Table 36 which are to be used for the calculation. However, experience with data from several plants indicated that the more likely cause of the discrepancy is the accuracy of the reported values of average plate thickness.

The use of ampere-hour on rectifiers might have value for monitoring or record keeping for some plants in lieu of measuring the area of the parts plated provided the average thickness plated is known or determined.

Records of plating voltage and ampere-hours on each rectifier (or watt-hours) plus thickness deposited might be correlated with watt-hours of electricity consumed per day or month with allowance for other electricity uses (lighting, pumps, etc) to estimate total plated area per day or month. The total effluent could be approximated by the plant water purchases if mainly for electroplating. Thus, the information on electric power consumption and water consumption from monthly bills for these

*The Guidebook and Directory for Metal Finishing (3) p. 426-429 gives a detailed description of methods for calculating area plated.

TABLE 36 TYPICAL CURRENT EFFICIENCIES ASSUMED FOR CALCULATION OF PLATED AREA USING EQUATION (2)

Type of Plating Operation	Typical Current Efficiency, percent	Constant (k) amp-hr/mm-sq m	Constant (k) amp-hr/mil-sq ft
Cyanide copper	50	3.75×10^3	8.84
Noncyanide copper	100	7.49×10^3	17.68
Nickel	100	8.05×10^3	19.00
Chromium	13	21.95×10^3	51.80
Cyanide zinc	60	5.80×10^3	13.70
Noncyanide zinc	100	5.80×10^3	13.70

services might be used in an approximation of daily plated area for a cross check against plated area determined by more direct means.

In practice, it should be possible for electroplaters to readily adapt to keeping records of plated area for reporting purposes. The fact that many platers do not presently know their production rate in terms of surface area plated is not a valid consideration since there has been no prior requirement to keep such records. Determining plated area should not be difficult for platers whose process operation is dependent on use of the correct current density for optimum plating results.

Total surface area is more closely related to dragout than plated area, and can generally be estimated once the plated area is known. If a part is plated on only one side the total surface area would be approximately twice the plated area. In barrel plating total surface area would be the same as plated area.

Application of Guidelines

Definition of Terms

To discuss the application of the guidelines it is first necessary to define several terms.

"Process";	A process is the accumulation of steps required to bring about a metal finishing result. An electroplating process includes cleaning and usually pickling of the basis metal, a strike if necessary, the plating step, and all rinses needed to carry out the process.
"Operation";	The term operation shall mean any step in the plating process in which copper, nickel, chromium, or zinc metal or chromate is deposited on a base material followed by a rinse. The processing steps of cleaning and pickling are not operations.
"Rinse";	A rinse is a step in a process used to remove components of a bath from the work following an operation. A rinse may consist of a sequence such as successive countercurrent rinsing or hot rinsing followed by cold rinsing with deionized water. Nevertheless, there is only one rinse after an operation.

In determining the allowable discharge of a pollutant, it is important to be able to count the number of operations in a process. In the following process there are two operations marked with asterisks.

- Alkaline Clean
- Rinse
- Acid Dip
- Rinse
- * Nickel Plate
- Rinse
- * Chromium Plate
- Rinse

The alkaline cleaning and acid dip steps are not operations even though they are followed by rinses. In effect, the rinse waters from these operations are considered a part of the rinse water following the first plating step (Nickel Plate) in considering water use.

In the following process the copper strike is not an operation since it is not followed by a rinse.

- Alkaline Clean
- Rinse
- Copper Cyanide Strike
- * Copper Cyanide Plate
- Rinse

Copper cyanide plating is the only operation.

Determination of Plated Area/Hr/Operation

The area for each line will be determined from information on the (1) average amperes used, (2) the sequence of plating operations, and (3) the average thickness in mil of each type of plate. If complete data on thickness is lacking, the following value will be used:

Copper	0.3 mil
Nickel	0.3 mil
Zinc	0.3 mil
Chromium	0.015 mil

Where chromating follows plating, the area will be the same as that of the primary plating operation. The equation:

$S = EIT/100\ kt$ (see page 173)

is then used to calculate plated area/hr/operation. In a line with several sequential operations, it is likely that the calculated plated areas for each plating operation will vary from each other although the actual area plated should be the same. The difference in calculated areas many vary by a factor of two or three. When applying the guidelines the figure used for area plated should be the arithmetic average of the calculated plated areas.

Where actual amperes are not known a value equal to 2/3 of the installed capacity for the line should be used. Where information on amperes is completely lacking for a line but water use is available, the sq m/hr may be determined by:

$$\text{Sq m/hr} = \frac{\text{l/hr used on the line}}{(200\ \text{l/sq m})(\text{no. of operations})}$$

$$\text{Sq ft/hr} = \frac{\text{gal/hr used on the line}}{(5\ \text{gal/hr})(\text{no. of operations})}$$

Once the plated area has been measured the guidelines can be used to determine the total allowable discharge of waste water constituents from the plant. Every time the surface is rinsed, following some operation in the process line, it is assumed that more waste water is produced, and a greater quantity of waste water constituents may be discharged under the guidelines. The cleaning and pickling rinses are therefore incorporated into the rinse following the first plating operation for purposes of calculating the allowable amount of waste water constituents discharged. The total allowable discharge in g/day will be:

$$(10^{-3})(\text{sq m plated /hr})(\text{effluent limitation in mg/sq m})\ (\text{No. of oper.})\ (\text{hr/day})$$

The total allowable discharge in lb/day is:

$$(10^{-6})(\text{sq ft plated/hr})(\text{effluent limitation in lb/million sq ft})\ (\text{No. of oper.})(\text{hr/day}) = \text{lb/day}$$

These relations hold for each effluent limitations guideline value listed in Table 1. The relations apply to each process line or part of a process line if the area plated/hr changes in the line.

The actual discharge from the plant is the product of the volume of effluent/hr and the concentration of waste water constituent in the effluent.

Thus,

$$\text{g/day} = (\text{liters/hr})(\text{mg/l})(10^{-3})(\text{hr/day})$$
$$\text{lb/day} = (8.33 \times 10^{-6})(\text{gal/hr})(\text{mg/l})(\text{hr/day})$$

Several examples will show how the guidelines are applied to specific processes.

Example 1. A process line is shown in Figure 33. The process consists of zinc plating on steel followed by chromating. The line plates an estimated 10 sq m/hr (107.6 sq ft/hr) of work and operates 8 hours/day. For purposes of this example, the plant will be considered to have only the one zinc plating line. Effluent volume from the waste treatment system is 1000 l/hr (264 gph). Concentrations of waste water constituents in the effluent are

Zinc	1.0 mg/l

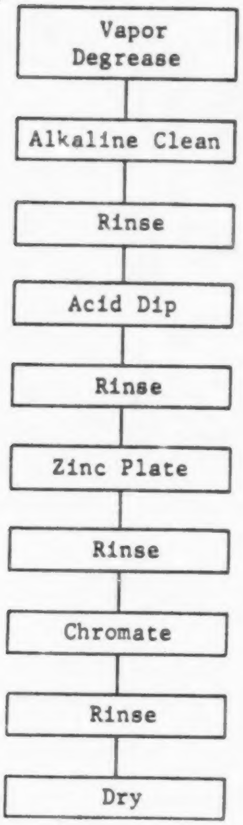

Vapor Degrease
Alkaline Clean
Rinse
Acid Dip
Rinse
Zinc Plate
Rinse
Chromate
Rinse
Dry

FIGURE 33 PROCESS LINE FOR EXAMPLE 1

Cyanide (total)	0.6 mg/l
Cyanide (oxidizable)	0.03 mg/l
Chromium (hexavalent)	0.05 mg/l
Chromium (total)	1.2 mg/l
TSS	15.

For purposes of calculating amount of discharge, the alkaline clean and acid dip steps are not counted; the zinc plating and chromating operations are counted to give a total of two.

Allowable Zn discharge = $(2.04 \times 10^{-6})(107.6)(16.4)(2)(8)$
$= 2.82 \times 10^{-2}$ lb/day

Actual Zn discharge = $(8.33 \times 10^{-6})(264)(1.0)$
$= 2.19 \times 10^{-3}$ lb/hr
$= (2.19 \times 10^{-4})(8)$
$= 1.76 \times 10^{-2}$ lb/day.

Effluent discharge for 8 hours is assumed. However, a composite sample taken over a different time span, i.e., 24 hours can be used to establish effluent concentrations and an average flow for the same time used. Therefore, the actual discharge of zinc is within the allowable limit. Allowable and actual limits for other waste water constituents are calculated in an identical manner. Results are as follows:

Constituent	Allowable Discharge, lb/day	Actual Discharge, lb/day
Zinc	2.82×10^{-2}	1.76×10^{-2}
Cyanide (total)	2.82×10^{-2}	1.06×10^{-2}
Cyanide (oxidizable)	2.82×10^{-3}	5.28×10^{-4}
Chromium (hexavalent)	2.82×10^{-3}	8.79×10^{-4}
Chromium (total)	2.82×10^{-2}	2.11×10^{-2}
TSS	1.13	8.43×10^{-1}

The effluent limitation guidelines are all met in this example since all actual discharges are below allowable discharges.

Example 2. A process line is shown in Figure 34. The process consists of plating steel with copper, nickel, and chromium. The line processes an estimated 20 sq m/hr (215 sq ft/hr) of work and operates 16 hours/day. For purposes of this example, the line will be considered the only one in the plant. Effluent volume from the waste treatment system is 6000 l/hr (1585 gph). Concentrations of waste water constituents in the effluent are:

Copper	0.5 mg/l
Nickel	1.3 mg/l
Chromium (hexavalent)	0.05 mg/l
Chromium (total)	1.2 mg/l
Cyanide (total)	0.6 mg/l
Cyanide (oxidizable)	0.03 mg/l
TSS	15.

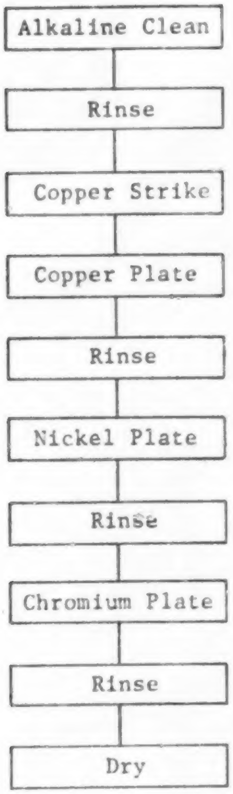

Alkaline Clean
Rinse
Copper Strike
Copper Plate
Rinse
Nickel Plate
Rinse
Chromium Plate
Rinse
Dry

FIGURE 34 PROCESS LINE FOR EXAMPLE 2

Note in Figure 34 that there is an alkaline cleaning, but no acid pickle. Thus, only the rinse after the alkaline cleaning step is omitted in counting operations. There is no rinse following the copper cyanide strike, and therefore this operation is not counted. The copper cyanide plating, nickel plating, and chromium plating operations have following rinses and are counted to give a total of three operations.

$$\begin{aligned}\text{Allowable Cu discharge} &= (10^{-6})(215)(16.4)(3)\\ &= 1.05 \times 10^{-2}\ \text{lb/hr}\\ &= (1.05 \times 10^{-2})(16)\\ &= 0.168\ \text{lb/day}\end{aligned}$$

$$\begin{aligned}\text{Actual Cu discharge} &= (8.33 \times 10^{-6})(1585)(0.5)\\ &= 6.60 \times 10^{-3}\ \text{lb/hr}\\ &= (3.30 \times 10^{-3})(16)\\ &= 0.105\ \text{lb/day.}\end{aligned}$$

Effluent flow for 16 hours a day is assumed, but a similar calculation can be made for values of concentration and flow average over 24 hours.

Therefore, the actual discharge of copper is within the allowable limit. Allowable and actual limits for other waste water constituents are calculated in an identical manner. Results are as follows:

Constituent	Allowable discharge, lg/day	Actual discharge, lb/day
Copper	0.168	0.105
Nickel	0.168	0.274
Chromium (hexavalent)	0.0168	0.0105
Chromium (total)	0.168	0.253
Cyanide (total)	0.168	0.126
Cyanide (oxidizable)	0.0168	0.006
TSS	6.74	3.16

In this example the guideline is exceeded by nickel and total chromium.

Example 3. This example will consider a plant made up of the line used in Example 1, plus the line used in Example 2. The effect of combining these two lines is to increase the allowable and actual discharge of constituents that originate in only one line. The reason for the increases is that the waste waters from both lines are brought together before final precipitation and clarification. Therefore, copper and nickel contaminate the waste water from the zinc plating line, and zinc contaminates the waste water from the copper-nickel-chrome line. The effect of the mutual dilution is to produce as much zinc discharge as if all waste water came from the zinc line, and as much nickel and copper discharge as if all waste water came from the copper-nickel-chrome line. Since chromium is a waste water constituent from both lines, the total discharge of this constituent is merely the sum of the effluent discharge from the separate lines. The statement is true the mutual dilution effect is not sufficient to bring the concentration of the waste water constituent below the value that can be obtained by precipitation. Normally, a 50- to 100-fold or greater dilution must be made which is unlikely where water conservation is practiced.

Where waste water from more than one line is combined, the waste water volume from each line is often not known, but only the total effluent volume. This will be 1,000 l/hr from the zinc line for 8 hours a day and 6,000 l/hr from the Cu-Ni-Cr line for 16 hours a day. Assume that the waste treatment plant operates 16 hours a day with effluent drainage of 6,500 l/hr (1717 gph). Concentrations of waste water constituents in the effluent are:

Zinc	1.0 mg/l
Copper	0.5 mg/l
Nickel	1.3 mg/l
Chromium (hexavalent)	0.05 mg/l
Chromium (total)	1.2 mg/l
Cyanide (total)	0.6 mg/l
Cyanide (oxidizable)	0.03
TSS	15.

The calculations for zinc are:

Allowable Zn discharge = $[(10^{-6})(16.4)][(107.6)(2)(8) + (215)(3)(16)] = 0.197$ lb/day

Actual Zn discharge = $(8.33 \times 10^{-6})(1717)(1.0)(16) = 0.228$

In the first calculation the result is the same as though zinc were plated on the second line rather than Cu-Ni-Cr since it makes no difference whether the zinc came from the plating operation or through contaminants of waste water from line 2 by zinc-containing waste water from line 1. The calculation assumes that after the zinc plating line has operated for 8 hours and is turned off, zinc contamination of the waste water from the Cu-Ni-Cr line continues for the additional hours that this line operates. This assumption is valid as long as the contamination exceeds the effluent concentration of 1.0 mg/l of zinc. The allowable discharge for zinc is exceeded when the two lines are combined in Example 3, while the zinc line operating by itself (Example 1) is able to stay within discharge limits. The larger water use per sq m in the Cu-Ni-Cr line is responsible for this difference. The results for other constituents may be summarized as follows:

Constituent	Allowable Discharge for single line lb/day	Allowable Discharge for combined lines lb/day	Actual Discharge for combined lines lb/day
Zinc	0.0280	0.197	.228
Copper	0.108	0.197	.114

Nickel	0.168	0.197	.297
Chromium (hexavalent)	0.00280/.0168	0.020	.011
Chromium (total)	0.0280/0.168	0.197	.275
Cyanide (total)	0.0280/0.168	0.197	.137
Cyanide (oxidizable)	0.00280/.0168	0.020	.006
TSS	1.13/674	7.88	3.43

Discharge from the combined lines exceeds the allowable amounts for zinc, nickel, and total chromium.

Example 4. Example 4 is that of a line that splits its operations at a point in the process. Thirty sq m/hr (323 sq ft/hr) are processed through the copper strike and plate. Twenty sq m/hr (215 sq ft/hr) are processed through semi-brite nickel and eventually through chrome plating. Ten sq m/hr (107.6 sq ft/hr) go directly from the copper plate rinse to brite nickel and chrome plate. The line operates 24 hours/day. The allowable discharge from this line is:

$$(10^{-6})[(323)(1) + (215)(3) + (107.6)(2)](24)(ELG) = \text{lb/day}$$

where ELG is the effluent limitation guideline for the specific waste water constituent. The 323 sq ft/hr of an operation go through one operation, copper plating. The 215 sq ft/hr go through three operations, and the 107.6 sq ft/hr go through three operations.

For copper:

$$(10^{-6})(16.4)(24)[(323)(1) + (107.6)(2) + (215)(3)] = .465 \text{ lb/day}$$

Constituent	Allowable Discharge, lb/day
Copper	0.465
Nickel	0.465
Chromium (hexavalent)	0.0465
Chromium (total)	0.465
Cyanide (total)	0.465
Cyanide (oxidizable)	0.0465
TSS	18.6

Actual discharges are the product of effluent flow and concentration, as in previous examples.

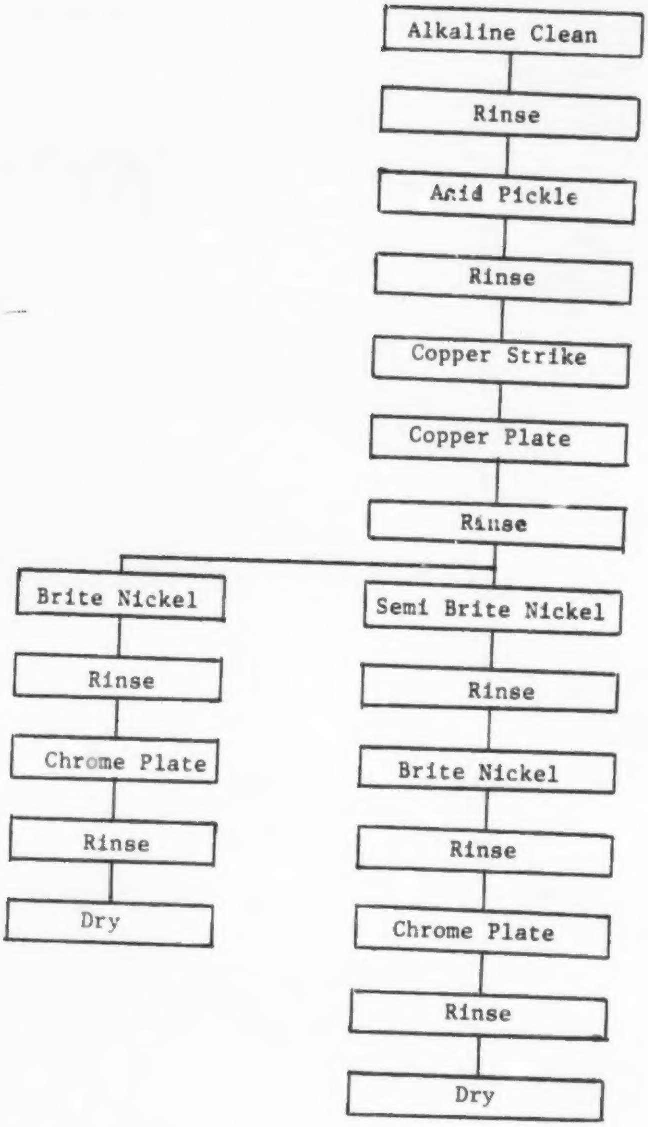

Alkaline Clean
Rinse
Acid Pickle
Rinse
Copper Strike
Copper Plate
Rinse
Brite Nickel
Rinse
Chrome Plate
Rinse
Dry
Semi Brite Nickel
Rinse
Brite Nickel
Rinse
Chrome Plate
Rinse
Dry

FIGURE 35 PROCESS LINE FOR EXAMPLE 4

SECTION X

BEST AVAILABLE TECHNOLOGY ECONOMICALLY ACHIEVABLE, GUIDELINES AND LIMITATIONS

Introduction

The effluent limitations which must be achieved by July 1, 1983 are to specify the degree of effluent reduction attainable through the application of the Best Available Technology Economically Achievable. This technology can be based on the very best control and treatment technology employed by a specific point source within the industry category and/or subcategory or technology that is readily transferable from one industry process to another. A specific finding must be made as to the availability of control measures and practices to eliminate the discharge of pollutants, taking into account the cost of such elimination.

Consideration must also be given to:

(a) the age of the equipment and facilities involved;

(b) the process employed;

(c) the engineering aspects of the application of various types of control technologies;

(d) process changes;

(e) cost of achieving the effluent reduction resulting from the technology;

(f) nonwater quality environmental impact (including energy requirements).

The Best Available Technology Economically Achievable also assesses the availability in all cases of in-process controls as well as the control or additional treatment techniques employed at the end of a production process.

A further consideration is the availability of processes and control technology at the pilot plant, semi-works, or other levels, which have demonstrated both technological performances and economic viability at a level sufficient to reasonably justify investing in such facilities. Best Available Technology Economically Achievable is the highest degree of control technology that has been achieved or has been demonstrated to be capable of being designed for plant scale operation up to and including no discharge of pollutants. Although economic factors are considered, the costs for this level of control are intended to be top-of-the-line of current technology subject to limitations imposed by economic and engineering feasibility.

However, Best Available Technology Economically Achievable may be characterized by some technical risk with respect to performance and with respect to certainty of costs and thus may necessitate some industrially sponsored development work prior to its application.

Industry Category and Subcategory Covered

The pertinent industry category is the electroplating industry as defined previously in Section IX.

Identification of Best Available Technology Economically Achievable

The Best Available Technology Economically Achievable is the use of in-process and end-of-process control and treatment to achieve no discharge of pollutants. By the use of in-process controls to reduce the volume of wastewater, it becomes economical to use end-of-process treatment designed to recover water and reuse the water within the plant thus avoiding any discharge of effluent to navigable waters. Solid constituents in the wastewater are disposed of to landfill or otherwise. As discussed in Sections VII and VIII one such type of treatment system that has been designed and is currently in operation supplements conventional chemical treatment with the use of reverse osmosis to recover water from the treated waste stream. Additional water is recovered for reuse by evaporation and distillation of the concentrated waste stream from the reverse osmosis unit. The concentrated wastewater solution from the evaporator is dry salt. It is expected that other methods will be developed during the next five years to avoid discharge of effluent to navigable waters and thus achieve no discharge of pollutants in an economical manner.

Rationale for Selection of Best Available Technology Economically Achievable

Time Available for Achieving Effluent Limitations

As noted previously, the effluent limitations selected for the Best Available Technology Economically Achievable for existing sources do not have to be achieved before July 1, 1983. This longer-range limitation allows sufficient time for retirement and replacement of existing electroplating and waste-treatment facilities as needed. Not all of these necessary changes can be expected by July 1, 1977 without placing an unjustifyable economic burden on those plants which are currently practicing pollution abatement.

Age of Equipment and Facilities

Replacement of older electroplating equipment and facilities will permit the installation of modern multitank countercurrent rinsing systems after each operation in each process line with conservation of water use for rinsing. The use of reclaim and recovery systems after each plating operation should be possible. Use of in-process controls to the maximum extent will reduce the volume of effluent such that recovery and reuse of water is economically attractive.

Process Employed

The application of the technology for end-of-process recovery and reuse of water to the maximum extent possible is not dependent on any significant change in the processes now used in the electroplating industry. Most water recovery technology can produce a higher quality of water than normally available from public or private water supplies. High purity water for the final rinse after plating is desirable to improve the quality of the electroplated product.

Engineering Aspects of the Application of Various Types of Control Techniques

Many plants are successfully using evaporative recovery systems after one or more plating operations with a net savings compared to chemical treatment. Evaporative systems are in current use after copper, nickel, chromium and zinc plating operations. Some plants have succeeded in using recovery systems after all plating operations in their facility. The engineering feasibility of in-process controls for recovery of chemicals and reuse of water are sufficiently well established. Sufficient operational use has been accumulated to reduce the technical risk with regard to performance and any uncertainty with respect to costs.

The technical feasibility of end-of-process water recovery systems has been established by extensive development of the recovery of pure water in many related industrial processes. Although some uncertainty may remain concerning the overall costs when applied to electroplating wastewaters, such uncertainty primarily relates to the volume of water that must be processed for recycling and reuse. The fact that the technology as applied to the electroplating industry has progressed beyond the pilot plant stage and has been designed and is being built for full-scale operational use indicates that the technology is available and probably economical.

Process Changes

Application of the technology is not dependent on any process changes. However, process changes and improvements are anticipated to be a natural consequence of meeting the effluent limitations in the most economic manner.

Cost of Achieving the Effluent Reduction

The costs of achieving no discharge of pollutants from large facilities electroplating copper, nickel, chromium, and zinc are expected to be no greater than $17.20/100 sq m ($16.00/1,000 sq ft) as discussed in Section VIII. With lower cost techniques, the cost for achieving no discharge of pollutants may be about the same as the cost for conventional chemical treatment, which averages about $10.70/100 sq m ($9.91/1,000 sq ft). The cost range for achieving no discharge of pollutants is expected to be only 4 to 6.5 percent of the plating costs. It may be possible to recover and reuse sufficient chemicals and water to offset the costs of achieving no discharge of pollutants in some plants.

Cost for small plants of achieving no discharge of wastewater pollutants to navigable waters are greater than $17.20/sq ft ($16.00/1,000 sq ft) as indicated in Table 22. Costs for small plants increase as size decreases because there is a minimum capital investment for equipment required to achieve reuse of water.

Nonwater Quality Environmental Impact

Application of technology to achieve no discharge of wastewater pollutants to navigable waters by July 1, 1983, will have little impact on the solid waste disposal problem with regard to metal removal as sludge beyond that envisioned to meet effluent limitations recommended for July 1, 1977.

In general, it is anticipated that the technology will be applied in a manner such that no discharge of effluent to surface waters occurs. Thus, all of the dissolved solids in the effluent which are primarily innocuous salts would be disposed of on land with suitable precaution to avoid any ground water contamination. Because these salts are not large in amount and can be dewatered to dry solids (by incineration if necessary) very little additional impact on the solid waste disposal problem is anticipated.

No impact on air pollution is expected as the result of achieving no discharge of pollutanzs to surface water. The available technology creates no air pollutants.

Energy requirements will increase with the achievement of no discharge of pollutants to surface water. The amount will vary from about 27 percent of the energy consumed by electroplating sources to as much as four times the energy needed for plating, depending on the specific process controls adopted in individual plants for achieving no discharge of pollutants.

Effluent Limitations Based on the Application of Best Available Technology Economically Achievable

The recommended effluent limitations to be achieved by July 1, 1983 for existing scurces based on the application of Best

Available Technology Economically Achievable is no discharge of wastewater pollutants to navigable waters.

Guidelines for the Application of Effluent Limitations

Achieving the effluent limitations of no discharge of wastewater pollutants by achieving no discharge of effluent to surface waters is the most direct method that eliminates the need for sampling and analysis. If there is other effluent discharge to surface waters from the plant not associated with electroplating, a determination is required that no wastewaters originating from electroplating processes are admixed with this other plant effluent.

SECTION XI

NEW SOURCE PERFORMANCE STANDARDS

Introduction

The standards of performance which must be achieved by new sources are to specify the degree of effluent reduction attainable through the application of higher levels of pollution control than those identified as Best Available Technology Economically Achievable for existing sources. The added consideration for new sources is the degree of effluent reduction attainable through the use of improved production processes and/or treatment techniques. The term "new source" is defined by the Act to mean "any source, the construction of which is commenced after publication of proposed regulations prescribing a standard of performance".

New Source Performance Standards are based on the best in-plant and end-of-process technology identified as Best Available Technology Economically Achievable for existing sources. Additional considerations applicable to new source performance standards take into account techniques for reducing the level of effluent by changing the production process itself or adopting alternative processes, operating methods, or other alternatives. The end result will be the identification of effluent standards which reflect levels of control achievable through the use of improved production processes (as well as control technology), rather than prescribing a particular type of process or technology which must be employed. A further determination must be made as to whether a standard permitting no discharge of pollutants is practicable.

Consideration must also be given to:

(a) the type of process employed and process changes
(b) operating methods
(c) batch as opposed to continuous operations
(d) use of alternative raw materials and mixes of raw materials
(e) use of dry rather than wet processes (including substitution of recoverable solvents for water)
(f) recovery of pollutants as by-products.

Standards of Performance for New Sources are based on applicable technology and related effluent limitations covering discharges directly into waterways.

Consideration must also be given to the fact that Standards of Performance for New Sources could require compliance about three years sooner than the effluent limitations to be achieved by existing sources by July 1, 1977. However, new sources should achieve the same effluent limitations as existing sources by July 1, 1983.

Preceding page blank

Industry Category and Subcategory Covered

The recommended new source performance standards cover the electroplating industry category as previously defined in Section IX.

Identification of Control and Treatment Technology Applicable to Performance Standards and Pretreatment Standards for New Sources

The technology previously identified in Section IX as Best Practicable Control Technology Currently Available is also applicable to New Source Performance Standards. In addition a new source can utilize the best practice in multitank rinsing after each operation in the process as required to meet the effluent limitations at the time of construction. Thus, with no practical restrictions on rinsewater conservation after each operation by multitank rinsing, there are fewer restrictions on the use of advanced techniques for recovery of plating bath chemicals and reduction of wastewater from rinsing after pre-treatment and posttreatment. Maximum use of combinations of evaporative, reverse osmosis, and ion exchange systems for in-process control currently available should be investigated. A small end-of-pipe chemical treatment system can be used to treat spills, concentrated solution dumps, and any other water flows not economically amenable to in-process water and chemical recovery.

The technology previously identified in Section X as Best Available Technology Economically Achievable is also applicable to New Sources to achieve zero discharge of pollutants to navigable waters at least by July 1, 1983, as required for existing sources.

Rationale for Selection of Control and Treatment Technology Applicable to New Source Performance Standards

The rationale for the selection of the above technology as applicable to new sources discharging to navigable waters is as follows:

(1) In contrast to an existing source, a new source has complete freedom to choose the most advantageous electroplating equipment and facility design to maximize water conservation by use of as many multitank rinsing operations as necessary. This, in turn, allows for economic use of in-process controls for chemical and water recovery and reuse.

(2) In contrast to an existing source which may have at

present a large capital investment in waste treatment facilities to meet effluent limitations by July 1, 1977, a new source has complete freedom in the selection of the Best Available Technology Economically Achievable in the design of new waste treatment facilities.

(3) In contrast to an existing source, a new source has freedom of choice with regard to geographic location in seeking any economic advantage relative to power cost or land cost.

Since the technology for achieving no discharge of pollutants has been demonstrated to be capable of being designed to achieve no discharge of effluent for a facility recently constructed, it is considered the best demonstrated technology currently available for some new sources. The possibility of a slightly higher cost in relation to several orders of magnitude reduction in pollution and the possible elimination of monitoring expense for no discharge of effluent warrants selection of this technology in defining the Standard of Performance for the electroplating industry to be achieved by July 1, 1983.

Consideration was given to the other factors listed in the Introduction to this Section pertinent to defining the control and treatment technology applicable to New Source Performance Standards. Based on information developed in Sections III through X of this report, it is evident that there are many more advantageous options available to a new source, relative to those available to an existing source. Thus a new source should achieve greater pollution reduction.

Standards of Performance Applicable to New Sources

The recommended Standards of Performance to be achieved by new sources discharging to navigable waters was shown previously in Table 2 of Section II.

The quantitative values for the 30-day average standard for each parameter in mg/sq m (lb/10^6 sq ft) is based on a nominal effluent factor of 80 l/sq m (1 gal/sq ft) combined with the concentrations achievable by chemical treatment as previously shown in Table 34 of Section IX for existing sources based on an effluent factor of 80 l/sq m. For example, 0.5 mg/l for copper, nickel, total chromium, zinc, and total cyanide, 0.05 mg/l for hexavalent chromium and oxidizable cyanide, 15 mg/l for suspended solids, when combined with an effluent factor of 80 l/sq m are the basis for the 30-day average standards of performance in Table 2.

In effect, Standards of Performance for New Sources Table 2 are one half the values of the Effluent Limitations for existing sources to achieve by July 1, 1977, as shown in Table 1. The rationale for selection of Standards of Performance is based on the technical feasibility of achieving greater reduction in water use by multitank rinsing at the time of construction of new facilities in contrast to the present limitations for some existing sources. For example, if an existing source can achieve an effluent factor of 160 l/sq m, a new source should be able to design a new facility to achieve an effluent factor of 80 l/sq m. As discussed previously in Section IX, the Standard of Performance in mg/sq m is the product of the plant effluent factor in l/sq m and the concentration of the parameter in the treated effluent in mg/l. The choice of whether to reduce concentration by emphasis on optimum chemical treatment and clarification or whether to reduce effluent volume by water conservation or a combination of both approaches is left to the discretion of the new source.

The rationale for establishing the daily maximum value of Standards of Performance at twice the 30-day average is based on the limitations in accuracy of analytical methods for measuring small concentrations, the usual 24-time lag after analysis for corrective action, the accuracy of measurement of effluent flow, and plated areas as discussed previously in Section IX.

It is recommended that new sources meet the same effluent limitations as required for existing sources by July 1, 1983, based on the effluent reduction believed to be attainable by the application of the Best Available Technology Economically Achievable.

Guidelines for the Application of New Source Performance Standards

The recommended guidelines for the application of Standards of Performance for New Sources discharging to navigable waters are the same as those in Section IX relating to existing sources based on use of the Best Practicable Control Technology Currently Available and those in Section X based on use of Best Available Technology Economically Achievable.

SECTION XII

ACKNOWLEDGEMENTS

The Environmental Protection Agency was aided in the preparation of this Development Document by Battelle Columbus Laboratories under the direction of William H. Safranek, Luther Vaaler, Jack Clifford. John Gurklis and Carl Layer on Battelle's staff made significant contributions.

Harry M. Thron, Jr. served as project officer on this study through the initial work with the contractor and development of the proposed document. His work was invaluable to the successful completion of the final document. Allen Cywin, Director, Effluent Guidelines Division, Ernst P. Hall, Deputy Director, Effluent Guidelines Division and Walter J. Hunt, Chief, Effluent Guidelines Development Branch, offered guidance and suggestions during this program.

The members of the working group/steering committee who coordinated the internal EPA review are:

Allen Cywin, Effluent Guidelines Division
Walter J. Hunt, Effluent Guidelines Division
Harry M. Thron, Effluent Guidelines Division
Kit R. Krickenberger, Effluent Guidelines Division
Edward Dulaney, Effluent Guidelines Division
Murray Strier, Office of Permit Programs
John Ciancia, NERC, Cincinnati, (Edison)
Hugh Durham, NERC, Corvallis (Grosse Ile)
Lew Felleison, Region III
Tom Gross, Office of Solid Waste Management Programs
Tim Fields, Office of Solid Waste Management Programs
Alan Eckert, Office of General Counsel
Swep Davis, Office of Planning and Evaluation

Acknowledgement and appreciation is also given to the secretarial staff of both the Effluent Guidelines Division and Battelle for their effort in the typing of drafts and necessary revisions, and the final preparation of this document:

Kaye Starr, Effluent Guidelines Division
Nancy Zrubek, Effluent Guidelines Division
Linda Rose, Effluent Guidelines Division
Brenda Holmone, Effluent Guidelines Division
Chris Miller, Effluent Guidelines Division
Sharon Ashe, Effluent Guidelines Division
Nancy Dunn, Battelle
Paula Thompson, Battelle
Terri Floyd, Battelle

Appreciation is extended to the following organizations associated with the electroplating industry:

- American Electroplaters Society
- duPont de Nemours and Company
- Heil Process Equipment Corporation
- Industrial Filter and Pump Manufacturing Company
- Ionic International, Inc.
- Lancy Laboratories
- M and T Chemicals, Inc.
- Metal Finishing Suppliers' Association, Inc.
- National Association of Metal Finishers
- Osmonics, Inc.
- Oxy Metal Finishing Corporation
- The Permutit Company
- Pfaudler Syhron Corporation

SECTION XIII

REFERENCES

(1) Safranek, W. H., "The Role of Design in Better Plating", Metal Progress, pp 67-70 (June 1968).

(2) Modern Electroplating, Edited by F. A. Lowenheim, Second Edition, John Wiley and Sons (1963), Chapter 7, pp 154-205.

(3) Metal Finishing Guidebook and Directory, Metals and Plastics Publications, Inc. (1973).

(4) "Methods for Chemical Analysis of Water and Wastes", Environmental Protection Agency, Water Quality Office, Cincinnati, Ohio (July 1971).

(5) Standard Methods for the Examination of Water and Wastewater, Thirteenth Edition (1971).

(6) ASTM Designation 2036-72.

(7) Ceresa, M., and Lancy, L. E., "Metal Finishing Waste Disposal. Part One", Metal Finishing, 66 (4), 56-62 (April 1968).

(8) Pourbaix, Marcel, Atlas of Electrochemical Equilibria in Aqueous Solutions, Pergamon Press, New York (1966).

(9) Marquardt, Kurt, "Erfahrungen mit Ionensautauschern als Endreinungsstufe nach Entgiftung- und Neutralisationsanlagen aller Art", Metalloberflache Angew. Elektrochemie 26 (11), 434 (1972).

(10) Personal communication from Dr. Coleman, Western Electric Company, Indianapolis, Indiana.

(11) Environmental Sciences, Inc., "Ultimate Disposal of Liquid Wastes by Chemical Fixation".

(12) Tripler, A. B., Cherry, R. H., Smithson, G. Ray, Summary Report on the Reclamation of Metal Values from Metal Finishing Waste Treatment Sludges", Battelle Columbus Laboratories report to Metal Finisher's Foundation, July 6, 1973.

(13) Dodge, B. F., and Zabban, W., "Disposal of Plating Room Wastes. III. Cyanide Wastes: Treatment With Hypochlorites and Removal of Cyanates", Plating, 38 (6), 561-586 (June 1951).

(14) Dodge, B. F., and Zabban, W., "Disposal of Plating Room

Wastes. III. Cyanide Wastes: Treatment with Hypochlorites and Removal of Cyanates. Addendum", Plating, 39 (4), 385 (April 1952).

(15) Dodge, B. F., and Zabban, W., "Disposal of Plating Room Wastes. IV. Batch Volatilization of Hydrogen Cyanide From Aqueous Solutions of Cyanides", Plating, 39 (10), 1133-1139 (October 1952).

(16) Dodge, B. F., and Zabban, W., "Disposal of Plating Room Wastes. IV. Batch Volatilization of Hydrogen Cyanide From Aqueous Solutions of Cyanides. Continuation", Plating, 39 (11), 1235-1244 (November 1952).

(17 Overflow", Chemical Week, 111 (24), 47 (December 13, 1972).

(18) Oyler, R. W., "Disposal of Waste Cyanides by Electrolytic Oxidation", Plating, 36 (4), 341-342 (April 1949).

(19) Kurz, H., and Weber, W., "Electrolytic Cyanide Detoxication by the CYNOX Process", Galvanotechnik and Oberflaechenschutz, 3, 92-97 (1962).

(20) "Electrolysis Speeds Up Waste Treatment", Environmental Science and Technology", 4 (3), 201 (March 1970).

(21) Thiele, H., "Detoxification of Cyanide-Containing Waste Water by Catalytic Oxidation and Adsorption Process", Fortschritte Wasserchemie Ihrer Grenzgebiete, 9, 109-120 (1968): CA, 70, 4054 (1969).

(22) Bucksteeg, W., "Decomposition of Cyanide Wastes by Methods of Catalytic Oxidation Absorption", Proceedings of the 21st Industrial Waste Conference, Purdue University Engineering Extension Series, 688-695 (1966).

(23) "Destroy Free Cyanide in Compact, Continuous Unit", Calgon Corporation advertisement, Finishers' Management, 18 (2), 14 (February 1973).

(24) Sondak, N. E., and Dodge, B. F., "The Oxidation of Cyanide Bearing Plating Wastes by Ozone. Part I", Plating, 48 (2), 173-180 (February 1961).

(25) Sonday, N. E., and Dodge, B. F., "The Oxidation of Cyanide Bearing Plating Wastes by Ozone. Part II", Plating, 48 (3), 280-284 (March 1961).

(26) Rice, Rip G., letter from Effluent Discharge Effects Committee to Mr. Allen Cywin, Effluent Guidelines Division, July 9, 1973.

(27) "Cyanide Wastes Might Be Destroyed at One-Tenth the Conventional Cost", Chemical Engineering, 79 (29), 20

(December 25, 1972).

(28) Manufacturers' Literature, DMP Corporation, Charlotte, North Carolina (1973).

(29) Ible, N., and Frei, A. M., "Electrolytic Reduction of Chrome in Waste Water", Galvanotechnik und Oberflaechenschutz, 5 (6), 117-122 (1964).

(30) Schulze, G., "Electrochemical Reduction of Chromic Acid-Containing Waste Water", Galvanotechnik, 58 (7), 475-480 (1967): CA, 68, 15876t (1968).

(31) Anderson, J. R., and Weiss, Charles O., "Method for Precipitation of Heavy Metal Sulfides", U. S. Patent No. 3,740,331, June 19, 1973.

(32) Lancy, L. E., and Rice, R. L., "Upgrading Metal Finishing Facilities to Reduce Pollution", paper presented at the EPA Technology Transfer Seminar, New York, N.Y. (December 1972).

(33) Electroplating Engineering Handbook, Edited by A. K. Graham, Third Edition, Van Nostrand Reinhold Company, New York (1971).

(34) Olsen, A. E., "Upgrading Metal Finishing Facilities to Reduce Pollution; In-Process Pollution Abatement Practices", paper presented at the EPA Technology Transfer Seminar, New York, N. Y. (December, 1972).

(35) Novotny, C. J., "Water Use and Recovery", Finishers' Management, 18 (2), 43-46 + 50 (February 1973).

(36) Rushmere, J. D., "Process for Brightening Zinc and Cadmium Electroplates Using an Inner Salt of a Quaternary Pyridine Carboxylic Acid and Composition Containing the Same", U. S. Patent 3,411,996, November 19, 1968.

(37) Ceresa, M., and Lancy, L. E., "Metal Finishing Waste Disposal. Part Two", Metal Finishing, 66 (5), 60-65 (May 1968).

(38) Ceresa, M., and Lancy, L. E., "Metal Finishing Waste Disposal. Part Three", Metal Finishing, 66 (6), 112-118 (June 1968).

(40) Brown, C. J., et al., "Plating Waste Recovery by Reciprocating-Flow Ion Exchange", Technical Conference of The American Electroplaters' Society, Minneapolis, Minnesota, June 18, 1973.

(41) Oh, C. B., and Hartley, H. S., "Recycling Plating Wastes by Vapor Recompression", Products Finishing, 36 (8), 90-96 (May 1972).

(42) Kolesat, T. J., "Employment of Atmospheric Evaporative Towers in the Electroplating Industry as a Means of Recycle and Waste Elimination", Technical Conference of The American Electroplaters' Society, Minneapolis, Minnesota, June 18, 1973.

(43) McLay, W. J., Corning Glass Company, Personal Communication.

(44) Spatz, D. D., "Industrial Waste Processing With Reverse Osmosis", Osmonics, Inc., Hopkins, Minnesota (August 1, 1971).

(45) Spatz, D. D., "Electroplating Waste Water Processing With Reverse Osmosis", Products Finishing, 36 (11), 79-89 (August 1972).

(46) Campbell, R. J., and Emmerman, D. K., "Recycling of Water From Metal Finishing Wastes by Freezing Processes", ASME Paper 72-PID-7 (March 1972).

(47) Campbell, R. J., and Emmerman, D. K., "Freezing and Recycling of Plating Rinsewater", Industrial Water Engineering, 9 (4), 38-39 (June/July 1972).

(48) Tcbcuwiner, Sidney B., "Investigation of Treating Electroplaters Cyanide Waste by Electrodialysis," EPA A-R2-73-287 December, 1973.

SECTION XIV

GLOSSARY

Acid Dip

An acidic solution for activating the workpiece surface prior to electroplating in an acidic solution, especially after the workpiece has been processed in an alkaline solution.

Acidity

The concentration of acid ions expressed as pH for a solution.

Act

The Federal Water Pollution Control Act Amendments of 1972.

Activator

Chemical substance, usually stannous chloride, that triggers the electroless deposition process on a nonconducting surface.

Addition Agent

Substance, usually an organic material, added to an electroplating solution to improve the properties of the electroplate.

Alkalinity

The concentration of base ions expressed as pH for a solution.

Allowable Water Use

The sum of water used for each plating process or the sum of water used for each necessary rinsing operation.

Ampere

Unit of electricity, amount of which is the current that will deposit silver at the rate of 0.0011180 gram per second.

Ampere-hours

Product of amperes of electricity being used and time of that use.

Anions

The negative charge ions in the solution, i.e., hydroxyl.

Anode

The electrode that takes electrons from the anions in solution (is connected to the positive terminal of the direct current source).

Automatic Plating

(1) full - plating in which the cathodes are automatically conveyed through successive cleaning and plating tanks.

(2) semi - plating in which the cathodes are conveyed automatically through only one plating tank.

Barrel Plating

Electroplating of workpieces in barrels (bulk).

Basis Metal or Material

That substance of which the workpieces are made and that receives the electroplate and the treatments in preparation for plating.

Best Available Technology Economically Achievable

Level of technology applicable to effluent limitations to be achieved by July 1, 1983, for industrial discharges to surface waters as defined by Section 301 (b) (2) (A) of the Act.

Best Practicable Control Technology Currently Available

Level of technology applicable to effluent limitations to be achieved by July 1, 1977, for industrial discharges to surface waters as defined by Section 301 (b) (1) (A) of the act.

BOD

Biochemical oxygen demand.

Bright Dip

A solution used to produce a bright surface on a metal.

Capital Costs

Financial charges which are computed as the cost of capital times the capital expenditures for pollution control. The cost of capital is based upon a weighed average of the separate costs of debt and equity.

Captive Operation

Electroplating facility owned and operated by the same organization that manufactures the workpieces.

Captive Plating Shops

Companies engaged in product fabrication and/or assembly and normally process approximately the same number of the same products per month. The volume of toxic wastes created by captive operations is expected to be more or less constant.

Carbon Bed Catalytic Destruction

A nonelectrolytic process for the catalytic oxidation of cyanide wastes using trickling filters filled with low-temperature coke.

Catalyst

Chemical substance, usually palladium chloride, in a dip solution to cause electroless deposition of a metal on a nonconducting surface.

Category and Subcategory

Divisions of a particular industry which possess different traits which affect waste treatability and would require different effluent limitations.

Cathode

The electrode (the workpieces in electroplating) that transfers electrons to the cations in the solution.

Cations

The positive-charge ions in the solution, i.e., the metal to be electrodeposited, hydrogen, copper, nickel, etc.

Chelate Compound

A compound in which the metal is contained as an integral part of a ring structure and is not readily ionized.

Chelating Agent

A compound capable of forming a chelate compound with a metal ion.

Chemical Recovery Systems

Chemical treatment of electroplating wastes utilizing (1) batch methods, (2) continuous methods, or (3) integrated procedures.

Chromium Catalyst

Plating bath constituent that in small amounts makes possible the continuing capability to electrodeposit chromium. Usually fluoride, fluorosilicate and/or sulfate.

Cleaner

Usually an alkaline solution pretreatment to remove surface soil such as oils, greases, and substrates chemically unrelated to the basis material.

Closed-Loop Evaporation System

A system used for the recovery of chemicals and water from a plating line. An evaporator concentrates flow from the rinse water holding tank. The concentrated rinse solution is returned to the plating bath, and distilled water is returned to the final rinse tank. The system is designed for recovering 100 percent of the chemicals, normally lost in dragout, for reuse in the plating process.

COD

Chemical oxygen demand.

Compatible Pollutants

Those pollutants which can be adequately treated in publicly owned treatment works without harm to such works.

Continuous Treatment

Chemical waste treatment operating uninterruptedly as opposed to batch treatment; sometimes referred to as flow through treatment.

Conversion Coating

A coating produced by chemical or electrochemical treatment of a metallic surface that gives a superficial layer containing a compound of the metal, for example, chromate coatings on zinc and cadmium, oxide coatings on steel.

Coulomb

Product of current in amperes and time in seconds. Thus, one coulomb is 1 ampere-second.

Coulombic

A term used to denote a relationship based in coulombs and electrochemical equivalents according to Faraday's Law.

Counterflow Rinsing

Series of rinses; usually three, in which water flow is from last to first rinse, thus counterflow to direction work loads move through the rinses.

d-c Power Source

Direct Current power source.

Decorative Chrome

Refers to the multilayer electroplate of copper + nickel + chromium in that order, on the basis material to provide the bright decorative appearance.

Deposit

The material formed on the electrode or workpiece surface, i.e., a metal in electroplating.

Depreciation

Accounting charges reflecting the deterioration of a capital asset over its useful life.

Dragout

The solution that adheres to the objects removed from a bath. More precisely defined as that solution which is carried past the edge of the tank.

Dual Nickel Plate

Two layers of nickel electroplate with different properties to enhance corrosion resistance and appearance under chromium electroplate. Requires two different nickel plating baths.

Effluent

The waste water discharged from a point source to navigable waters.

Effluent Limitation

A maximum amount per unit of production of each specific constituent of the effluent that is subject to limitation in the discharge from a point source.

Electrochemical Equivalent

The weight of metal electrodeposited (or other substance changed chemically by reduction or oxidation) per unit of time and unit of current; i.e., pound per ampere-hour, grams per ampere-second.

Electrode

Conducting material for passing the electric current out of a solution by taking up or into it by giving up electrons from or to ions in the solution.

Electrodeposition

The transfer of electrons from the cathode to metal ions at its surface to produce the metal on the cathode surface.

Electroforming

The production or reproduction of articles by electrodeposition upon a mandrel or mold that is subsequently separated from the deposit.

Electroless Plating

Deposition of a metallic coating by a controlled chemical reduction that is catalyzed by the metal or alloy being deposited.

Electrolysis

The passage of current through an electrolyte bringing about chemical reactions.

Electrolytic Cell

A unit apparatus in which electrochemical reactions are produced by applying electrical energy, or which supplies electrical energy as a result of chemical reactions and which includes two or more electrodes and one or more electrolytes contained in a suitable vessel.

Electrolytic Decomposition

An electrochemical treatment used for the oxidation of cyanides. The method is practical and economical when applied to concentrated solutions such as contaminated baths, cyanide dips, stripping solutions, and concentrated rinses. Electrolysis is carried out at a current density of 35 amp/sq ft at the anode and 70 amp/sq ft at the cathode. Metal is deposited at the cathode and can be reclaimed.

Electroplating

The electrodeposition of an adherent metallic coating upon the basis metal or material for the purpose of securing a surface with properties or dimensions different from those of the basis metal or material.

Electroplating Process

An electroplating process includes a succession of operations starting with cleaning in alkaline solutions, acid dipping to neutralize or acidify the wet surface of the parts, followed by electroplating, rinsing to remove the processing solution from the workpieces, and drying.

Exhaust Wash

Water used to trap droplets and solubles from air passed to remove spray, vapor, and gasses from electroplating and process tanks.

Faraday

The number of coulombs (96,490) required for an electrochemical reaction involving one chemical equivalent.

Free Cyanide

(1) true - the actual concentration of cyanide radical, or equivalent alkali cyanide, not combined in complex ions with metals in solutions.

(2) calculated - the concentration of cyanide, or alkali cyanide, present in solution in excess of that calculated as necessary to form a specified complex ion with a metal or metals present in solution.

(3) analytical - the free cyanide content of a solution as determined by a specified analytical method.

Hard Chrome

Chromium electroplate applied for nondecorative use such as wear resistance in engineering applications.

Immersion Plate

A metallic deposit produced by a displacement reaction in which one metal displaces another from solution, for example:

$Fe + Cu^{++}$ T $Cu + Fe^{++}$

Incompatible Pollutants

Those pollutants which would cause harm to, adversely affect the performance of, or be inadequately treated in publicly owned treatment works.

Independent Operation

Job shop or contract shop in which electroplating is done on workpieces owned by the customer.

Integrated Chemical Treatment

A waste treatment method in which a chemical rinse tank is inserted in the plating line between the process tank and the water rinse tank. The chemical rinse solution is continuously circulated through the tank and removes the dragout while reacting chemicals with it.

Investment Costs

The capital expenditures required to bring the treatment or control technology into operation. These include the traditional expenditures such as design; purchase of land and materials;

etc.; plus any additional expenses required to bring the technology into operation including expenditures to establish related necessary solid waste disposal.

Joint Treatment

Treatment in publicly owned treatment works of combined municipal wastewaters of domestic origin and wastewaters from other sources.

Mandrel

A form used as a cathode in electroforming; a mold or matrix.

New Source

Any building, structure, facility, or installation from which there is or may be a discharge of pollutants and whose construction is commenced after the publication of the proposed regulations.

New Source Performance Standards

Performance standards for the industry and applicable new sources as defined by Section 306 of the Act.

Ohm

The unit of electrical resistance. The resistance at OC of a column of mercury of uniform cross section, having a length of 106.300 cm and a mass of 14.4521 gm.

Open-Loop Evaporation System

A system used for the partial recovery of chemicals and water from a plating line using less than 3 rinses. The circulation loop through the evaporator is opened by creating another flow path resulting in wastewater. A small percentage (4-5 percent) of the dragout that accumulates in the final rinse is not recirculated to the evaporator and must be treated by a chemical method before disposal.

ORP Recorders

Oxidation-reduction potential recorders.

Oxidizable Cyanide

Cyanide amenable to oxidation by chlorine according to standard analytical methods.

pH

A unit for measuring acidity or alkalinity of water, based on hydrogen ion concentrations. A pH of 7 indicates a "neutral" water or solution. At pH lower than 7, a solution is acidic. At pH higher than 7, a solution is alkaline.

Pickle

An acid solution used to remove oxides or other compounds related to the basis metal from its surface of a metal by chemical or electrochemical action.

Pickling

The removal of oxides or other compounds related to the basis metal from its surface by immersion in a pickle.

Plated Area

The area of the workpiece receiving an electrodeposit. The thickness of deposit usually varies over the plated area.

Plating Barrel

Container in which parts are placed loosely, so they can tumble as the barrel rotates in the plating or processing solution.

Plating Rack

Fixture that permits moving one or more workpieces in and out of a treating or plating tank and transferring electric current to the workpieces when in the tank.

Point Source

A single source of water discharge such as an individual plant.

Preplating Treatment Waste

Waste contributed by preplating treatments is affected by the basis materials, any surface soil on the workpieces, formulation of solutions used for cleaning or activating the materials, solution temperatures, and cycling times.

Pretreatment

Treatment performed in wastewaters from any source prior to introduction for joint treatment in publicly owned treatment works.

Rack Plating

Electroplating of workpieces on racks.

Reclaim Rinses

Reclaim rinses are used as the first step following a plating process to retain as much of the chemicals as possible and to allow return of the dragout solution to the plating tank.

Rectifier

A device which converts ac into dc by virtue of a characteristic permitting appreciable flow of current in only one direction.

Reverse Osmosis

A recovery process in which the more concentrated solution is put under a pressure greater than the osmotic pressure to drive water across the membrane to the dilute stream while leaving behind the dissolved salts.

Rinse

Water for removal of dragout by dipping, spraying, fogging, etc.

Rochelle Salt

Sodium potassium tartrate: KNaC4H4O6.4H2O.

Running Rinse

A rinse tank in which water continually flows in and out.

Save Rinse

Same as reclaim rinse.

Still Rinse

Does not have water flowing in and out as a running rinse and may be a reclaim rinse or dumped periodically to wastewater.

Standard of Performance

A maximum weight discharged per unit of production for each constituent that is subject to limitation and applicable to new sources as opposed to existing sources which are subject to effluent limitations.

Strike

(1) noun - a thin coating of metal (usually less than 0.0001 inch in thickness) to be followed by other coatings.

(2) noun - a solution used to deposit a strike.

(3) verb - to plate for a short time, usually at a high initial current density.

Tank

Term for vessel that contains the solution and auxiliary equipment for carrying out the electroplating or other operational step.

Tank Current

Total amperage required to electroplate all the workpieces of a tank load.

Tank Load

Total number of workpieces being processed simultaneously in the tank.

Total Chromium

Total chromium (CrT) is the sum of chromium in all valences.

Total Cyanide

The total content of cyanide expressed as the radical CN-, or alkali cyanide whether present as simple or complex ions. The sum of both the combined and free cyanide content of a plating solution. In analytical terminology, total cyanide is the sum of cyanide amenable to oxidation by chlorine and that which is not according to standard analytical methods.

Total Metal

Total metal is the sum of the metal content in both soluble and insoluble form.

Unit Operation

A single, discrete process as part of an overall sequence, e.g., precipitation, settling, filtration.

Used Current

Current that is used in electroplating operations and related to (1) the area being pla##d for a particular deposit thickness and (2) the processing time (area per unit time).

Volt

The voltage which will produce a current of one ampere through a resistance of one ohm.

Watt

An energy rate of one joule per second, or the power of an electric current of one ampere with an intensity of one volt.

Workpiece

The item to be electroplated.

TABLE 36

METRIC UNITS

CONVERSION TABLE

MULTIPLY (ENGLISH UNITS)		by	TO OBTAIN (METRIC UNITS)	
ENGLISH UNIT	ABBREVIATION	CONVERSION	ABBREVIATION	METRIC UNIT
acre	ac	0.405	ha	hectares
acre - feet	ac ft	1233.5	cu m	cubic meters
British Thermal Unit	BTU	0.252	kg cal	kilogram-calories
British Thermal Unit/pound	BTU/lb	0.555	kg cal/kg	kilogram calories/ kilogram
cubic feet/minute	cfm	0.028	cu m/min	cubic meters/minute
cubic feet/second	cfs	1.7	cu m/min	cubic meters/minute
cubic feet	cu ft	0.028	cu m	cubic meters
cubic feet	cu ft	28.32	l	liters
cubic inches	cu in	16.39	cu cm	cubic centimeters
degree Fahrenheit	°F	0.555(°F-32)*	°C	degree Centigrade
feet	ft	0.3048	m	meters
gallon	gal	3.785	l	liters
gallon/minute	gpm	0.0631	l/sec	liters/second
horsepower	hp	0.7457	kw	killowatts
inches	in	2.54	cm	centimeters
inches of mercury	in Hg	0.03342	atm	atmospheres
pounds	lb	0.454	kg	kilograms
million gallons/day	mgd	3,785	cu m/day	cubic meters/day
mile	mi	1.609	km	kilometer
pound/square inch (gauge)	psig	(0.06805 psig +1)*	atm	atmospheres (absolute)
square feet	sq ft	0.0929	sq m	square meters
square inches	sq in	6.452	sq cm	square centimeters
tons (short)	ton	0.907	kkg	metric tons (1000 kilograms)
yard	yd	0.9144	m	meters

* Actual conversion, not a multiplier

☆U.S. GOVERNMENT PRINTING OFFICE: 1974 546-318/345 1-3